Simulation of inelastic spin flip excitations and Kondo effect in STM spectroscopy of magnetic molecules on metal substrates

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Abstract

Single-ion magnetic anisotropy in molecular magnets leads to spin flip excitations that can be measured by inelastic scanning tunneling microscope (STM) spectroscopy. Here I present a semi ab initio scheme to compute the spectral features associated with inelastic spin flip excitations and Kondo effect of single molecular magnets. To this end density functional theory calculations of the molecule on the substrate are combined with more sophisticated many-body techniques for solving the Anderson impurity problem of the spin-carrying orbitals of the magnetic molecule coupled to the rest of the system, containing a phenomenological magnetic anisotropy term. For calculating the STM spectra an exact expression for the $dI/dV$ in the ideal STM limit, when the coupling to the STM tip becomes negligibly small, is derived. In this limit the $dI/dV$ is simply related to the spectral function of the molecule–substrate system. For the case of an Fe porphyrin molecule on the Au(111) substrate, the calculated STM spectra are in good agreement with recently measured STM spectra, showing the typical step features at finite bias associated with spin flip excitation of a spin-1 quantum magnet. For the case of Kondo effect in Mn porphyrin on Au(111), the agreement with the experimental spectra is not as good due to the neglect of quantum interference in the tunneling.

Keywords: magnetic molecules, strong electronic correlations, Kondo effect, inelastic spin flip excitations, scanning tunneling microscope spectroscopy

(Some figures may appear in colour only in the online journal)

1. Introduction

The electronic and magnetic properties of nanoscale quantum magnets, such as magnetic atoms, clusters and molecules on conducting substrates, can be strongly affected by their environment, and can be investigated by means of scanning tunneling microscopy (STM) [1]. Specifically, STM spectroscopy (STS) allows to measure the electronic and magnetic excitations of nanoscale systems [2–5]. For example, step features at finite bias voltages in the differential conductance ($dI/dV$) spectra measured by STS can be related to inelastic spin flip excitations, associated with the magnetic anisotropy of the nanoscale magnet [6–9]. On the other hand, the appearance of a zero-bias anomaly in the STM spectrum points to a Kondo effect (see e.g. the book by Hewson [10]) due to a degenerate magnetic ground state screened by the conduction electrons [11–13]. Both phenomena have also been observed simultaneously, for example in the case of Co on CuN substrates, where the magnetic anisotropy leads to a splitting of the spin-3/2 ground state into two doublet states [14, 15]. Moreover, interesting information about the system is also encoded in the actual lineshapes of the spectral features associated with both phenomena in the measured $dI/dV$ spectra. For example, a Kondo resonance gives rise to a zero-bias anomaly that is generally well described by a Fano lineshape.
[12, 13, 16] or a generalized Frota lineshape [17, 18]. The actual shape of this Fano/Frota feature reveals information about the spin-carrying orbitals involved in the Kondo effect [19], or the voltage drop within a molecular junction [18]. Similarly, the actual lineshapes of the spin flip excitation steps in STS of magnetic porphyrin molecules on metal substrates contains information about the orbitals involved in the spin flip excitations [20].

On the theory side, most of the phenomenology of STM spectroscopy of nanoscale quantum magnets on conducting substrates can be described in terms of Kondo type and Anderson type impurity models, which capture the Kondo effect as well as spin flip excitations by inclusion of a magnetic anisotropy term into the model [7–9, 15, 21–26]. In combination with experiments these model Hamiltonian calculations have revealed interesting effects such as the renormalization of single-ion magnetic anisotropy by Kondo exchange coupling to the conduction electrons [15, 27]. Ab initio density functional theory (DFT) calculations, on the other hand, yield valuable insights about the molecular orbitals hosting the spin and the charging state of the molecule [20, 28], but cannot account for the dynamic correlations1 that give rise to Kondo effect and spin flip excitations.

By combining ab initio DFT calculations with impurity model calculations, it is possible to gain further insights into the often rather complex situation encountered in real nanoscale systems [29–37]. For example, DFT plus impurity solver calculations attribute the Kondo resonances in the STS of manganese phthalacyanine (MnPc) on the lead substrate and of manganese porphyrin on gold to underscreened Kondo effects in the Mn 2z2-orbital, strongly influenced by charge fluctuations [18, 31]. Also the Fano lineshape in the STS measured for the Co on Cu(001) could be attributed in this way to a Kondo peak in the Co 2z2-orbital [19, 32].

In these cases the low-bias transport characteristics can be straight forwardly calculated in the phase coherent approximation from the correlated transmission function [29, 32, 37], which takes into account quantum interference effects as well as elastic many-body effects such as the Kondo effect, leading e.g. to Fano behavior in the dI/dV. On the other hand, inelastic electron scattering resulting from electron–electron interactions is neglected in this approach [37]. While in the case of the Kondo effect, the inelastic corrections to the low-bias transport properties are actually very small [38], this is naturally not the case for the inelastic spin flip excitations, for which inelastic many-body scattering plays of course a crucial role. In principle one would thus have to make use of the Meir–Wingreen equation for computing the current via a nanoscopic region [39]. This requires to solve the many-body problem out of equilibrium which is in general a difficult and computationally very demanding task.

Instead here we make use of an exact limit of the Meir–Wingreen equation when the coupling to the STM tip becomes very weak compared to the coupling to the substrate and all the applied voltage drops at the STM tip [40]. In this ideal STM limit the molecule is in quasi equilibrium with the substrate, and the dI/dV can be expressed simply in terms of the equilibrium spectral function of the molecule. For finite but small coupling to the STM tip the ideal STM limit becomes an approximation, that captures elastic (e.g. Kondo effect) as well an inelastic (e.g. spin flip excitations) many-body effects encoded in the spectral function, but neglects quantum interference phenomena in the tunneling from the tip to the molecule.

The paper is organized as follows: in section 2 the methodology for computing the STM spectra of magnetic molecules on conducting substrates is introduced. A special focus lies on the derivation of the ideal STM limit (section 2.2). In section 3 the methodology is applied to the calculation of the electronic structure and STM spectra of Fe and Mn porphyrin molecules on the Au(1 1 1) substrate. Similar systems only differing by the type of ligands have been recently measured in a number of experiments [18, 20, 28, 41]. In section 4 the paper concludes with a couple of general remarks regarding the results and methodology.

2. Methodology

2.1. Setup

We consider the situation schematically depicted in figure 1: a molecule (M) deposited on a metal substrate (S) is coupled weakly to a second electrode, the STM tip (T), which serves as a probe. The T electrode couples also weakly to part of the surface in the proximity of M. We thus define a central region (C) which contains M and the part of the surface coupled to T. We assume that electron–electron interactions only take place

Figure 1. Left: schematic drawing of typical STM setup for probing a molecule. The STM tip (T) probes the central region (C) consisting of the molecule (M) and part of the substrate. The coupling ΓC of C to the STM tip T is usually much weaker than the coupling ΓS to the rest of the substrate (S), ΓC ≪ ΓS. Right: the DFT calculations are done for the bigger device region (D) which includes a small portion of the STM tip T in addition to the central region C. This setup allows to determine the coupling matrix ΓT from first principles (see text for further explanations).

\[ \text{Figure 1. Left: schematic drawing of typical STM setup for probing a molecule. The STM tip (T) probes the central region (C) consisting of the molecule (M) and part of the substrate. The coupling } \Gamma_C \text{ of C to the STM tip T is usually much weaker than the coupling } \Gamma_S \text{ to the rest of the substrate (S), } \Gamma_C \ll \Gamma_S. \text{ Right: the DFT calculations are done for the bigger device region (D) which includes a small portion of the STM tip T in addition to the central region C. This setup allows to determine the coupling matrix } \Gamma_T \text{ from first principles (see text for further explanations).} \]
in the central region, while the electrons in the two electrodes T and S are (effectively) non-interacting.

The Hamiltonian of the central region coupled to the two electrodes S and T is thus given by

$$\hat{H} = \hat{H}_C + \hat{H}_S + \tilde{V}_S + \tilde{H}_T + \tilde{V}_T$$  \hspace{1cm} (1)

where $\hat{H}_C$ is the Hamiltonian of the central region, which comprises a general electron–electron interaction term:

$$\hat{H}_C = \sum_{i,j,\sigma} (\hat{H}_{ij}^{C})_{ij} \hat{d}_i^{\dagger} \hat{d}_j + \frac{1}{2} \sum_{i,j,l,\sigma} V_{ijl} \hat{d}_i^{\dagger} \hat{d}_j^{\dagger} \hat{d}_l \hat{d}_l^{\dagger}$$  \hspace{1cm} (2)

where $\hat{H}_{ij}^{C}$ is the one-body part of the Hamiltonian (in matrix notation) and $V_{ijl}$ are the matrix elements of the Coulomb interaction.

Electrode $\alpha$ ($\alpha \in \{T, S\}$), is described by the Hamiltonian

$$\hat{H}_\alpha = \sum_{i,\sigma} (\hat{H}_{i\alpha})_{i\sigma} \hat{d}_i^{\dagger} \hat{d}_i + \mu_\alpha \hat{c}_\alpha^{\dagger} \hat{c}_\alpha$$

where we have also included the chemical potential $\mu_\alpha$ applied to electrode $\alpha$, which describes the electrostatic shift of the electrode band structure induced by the chemical potential. The coupling between C and electrode $\alpha$ is described by

$$\tilde{V}_\alpha = \sum_{i,k,h} (\tilde{V}_{i\alpha})_{ih} \hat{d}_i^{\dagger} \hat{d}_h + \text{h.c.}$$

The retarded Green’s function (GF) of the central region can now be written as

$$G_C(\omega) = \left( \omega - H_0^c - \Sigma_C(\omega) - \Sigma_T(\omega) - \Sigma_S(\omega) \right)^{-1}$$  \hspace{1cm} (3)

where $\Sigma_C(\omega)$ is the many-body self-energy describing the effect of electron–electron interactions within region C. $\Sigma_{\alpha}(\omega)$ for $\alpha \in \{T, S\}$ on the other hand are the so-called embedding self-energies given by

$$\Sigma_\alpha(\omega) = V_{\alpha}^d \left( \frac{1}{\omega - \mu_\alpha - \hat{H}_\alpha} V_{\alpha} \right)$$  \hspace{1cm} (4)

which describe the coupling of C to the conduction electron bath in the two electrodes. The anti-hermitian part of the embedding self-energies yields the so-called coupling matrices, $\Gamma_\alpha = i [\Sigma_\alpha^d - \Sigma_\alpha]$, which describe the broadening of the central region due to the coupling to the electrodes.

### 2.2. The ideal STM limit

By applying a bias voltage $eV = \mu_T - \mu_S$ between the STM tip and the substrate a current $I$ is driven through the molecular junction. In the ideal limit of very weak coupling to the STM tip ($\Gamma_T \ll \Gamma_S$) and for the applied voltage dropping entirely at the STM tip ($\mu_T = eV$ and $\mu_S = 0$), the differential conductance $dI/dV$ can be directly related to the equilibrium many-body spectral function of C, $A_C(\omega) = -2\text{Im} G_C(\omega)$ [40]. The key observation is that in the ideal STM limit, $\Gamma_T \to 0$, the non-equilibrium GFs of the central region become independent of the applied bias $V$, i.e. the C region is essentially in equilibrium with the substrate. Hence the lesser GF of C reduces to its equilibrium value, $iG_C^R(\omega) \to f_s(\omega)A_C(\omega)$ for $\Gamma_T \to 0$, where $f_s(\omega) = f(\omega)$ is the Fermi function for the substrate, which does not depend on the bias.

The Fermi function of the STM tip, on the other hand, is given by $f_T(\omega) = f(\omega - eV)$. In the ideal STM limit, the tunneling current from the tip electrode to the central region given by the Meir–Wingreen expression [39]

$$I = \frac{2e}{h} \int d\omega \text{Tr} \left\{ \Gamma_T(\omega) [f_T(\omega) A_C(\omega) + iG_C^R(\omega)] \right\}$$  \hspace{1cm} (5)

thus reduces to

$$I \to 0 \Rightarrow \frac{2e}{h} \int d\omega \left[ f_T(\omega) + f_S(\omega) \right] \text{Tr} \left\{ \Gamma_T(\omega) A_C(\omega) \right\}.$$  \hspace{1cm} (6)

Taking the derivative w.r.t. the bias $V$ then yields

$$\frac{dI}{dV} = \frac{2e^2}{h} \int d\omega [-f'(\omega - eV)] \text{Tr} \left\{ \Gamma_T(\omega) A_C(\omega) \right\}.$$  \hspace{1cm} (7)

Finally, in the zero temperature limit, $-f'(\omega) \to \delta(\omega)$, and hence in the ideal STM limit ($\Gamma_T, T \to 0$) at zero temperature, we obtain the following expression that relates the differential conductance directly to the equilibrium many-body spectral function of the central region:

$$\frac{dI}{dV} = \frac{2e^2}{h} \text{Tr} \left\{ \Gamma_0^T A_C(eV) \right\}$$  \hspace{1cm} (8)

where $\Gamma_0^T$ is the equilibrium tip coupling matrix (i.e. for $\mu_T = 0$), evaluated at the Fermi level ($\omega = 0$), since $\Gamma_T(eV) = -2\text{Im} \frac{V_T}{eV - eV - H_T} - V_T \equiv \Gamma_0^T$ due to the electrostatic shift of the tip band structure by $\mu_T = eV$.

Equation (8) is essentially a generalization of the Tersoff–Hamann result for the description of electron tunneling in STM experiments [42] to the case of orbital-dependent coupling to the STM tip (i.e. non-constant tunneling matrix elements). Also note that (8) represents an exact limit of the Meir–Wingreen equation, fully taking into account interaction effects in the central region, encoded in the many-body spectral function $A_C(\omega)$. Of course, for a realistic STM setup $\Gamma_T$ is finite, and hence (8) is actually an approximation, although a very good one, as the tip coupling $\Gamma_T$ is usually orders of magnitude smaller than the coupling to the substrate $\Gamma_S$ (see also below) due to the exponential dependence of the tunneling matrix elements on the distance to the sample.

### 2.3. DFT+ Anderson impurity solver calculations

In order to calculate the $dI/dV$ we have thus to compute the spectral function of the central region, taking into account the coupling to the substrate and interaction effects in C. Here we make use of the nanoscale system dynamical mean-field theory (NanoDMFT) approach which combines mean-field like Kohn–Sham (KS) DFT calculations for the interacting region C with a more sophisticated many-body treatment for a small portion of the system using an Anderson impurity solver technique, in order to take into account dynamic correlation effects arising from strong electronic interactions, e.g. within the 3d-shell of a transition metal atom [29, 32]. In the case of several Anderson impurities in the central region, NanoDMFT can be employed [43].

As we also have to determine the coupling $\Gamma_T$ to the STM tip, it is convenient to include part of the STM tip into the DFT calculation, even though the coupling of the central region
to the STM tip is weak, and thus does not really influence its electronic structure. Hence we extend the central region and include a small part of the tip electrode T into the larger device region (D), as depicted schematically in the right panel of figure 1. In a first step, the electronic structure of the device region D is then calculated on the DFT level, taking into account the coupling to the substrate S and the rest of the tip electrode T using the ANT.G package [44] in connection with the Gaussian99 quantum chemistry code [45], as described in more detail in previous in work [46]. This yields the KS GF of the device region

\[ G^D_{\text{ks}}(\omega) = \left(\omega - H^D_0 + V_{\text{Hxc}} - \Sigma^D_T(\omega) - \Sigma^S_S(\omega)\right)^{-1} \]  

where \( H^D_0 \) is the one-body part of the Hamiltonian of the device region and \( V_{\text{Hxc}} \) is the Hartree exchange–correlation (Hxc) potential which yields an effective mean-field description of the interactions within D. \( \Sigma^T_T \) is the embedding self-energy describing the coupling of a small part of the STM tip T included in D to the rest of the STM tip T', and \( \Sigma^S_S \) the embedding self-energy describing the coupling of C to the rest of the surface S, as before. The self-energy \( \Sigma_T \) and corresponding coupling matrix \( \Gamma_T \) can now be calculated from the projection of the KS device GF onto the tip atoms included in D, \( G^T_{\text{ks}}(\omega) = P_T G^D_{\text{ks}}(\omega) P_T \), as

\[ \Sigma_T(\omega) = V^T_T G^T_{\text{ks}}(\omega) V_T \]  

where the hopping matrix \( V_T \) is obtained from the off-diagonal projection of the KS Hamiltonian, \( H^T_0 = H^D_0 + V_{\text{Hxc}} \) on the T and C parts of the device region: \( V_T = P_T H^D_0 P_C \).

The static mean-field picture of the KS DFT calculation does not account for so-called dynamic correlation effects originating from strong electronic interactions e.g. in the open \( d \)-shells of transition metal (TM) atoms, or the \( f \)-shells of lanthanide or actinide atoms. Dynamic correlations give rise for example to the Kondo effect and are important for the description of spin flip excitations of magnetic atoms and molecules on conducting substrates [15, 25, 26]. In the next step, we thus perform a projection onto the strongly correlated subspace, which in our case is given by the 3\( d \)-shell of a transition metal (TM) atom at the center of the molecule. This yields an Anderson impurity model (AIM) describing the 3\( d \)-shell coupled to the substrate and to the rest of the molecule. In order to take into account dynamic correlations beyond the mean-field description, the 3\( d \)-shell is augmented by an (effective) Coulomb interaction term. The Hamiltonian of the 3\( d \)-shell thus reads:

\[ H_{3d} = \sum_{i,j,\sigma} h_{ij}^{3d} d_i^{\dagger} d_j + \sum_{i,j,\sigma} U_{ij} d_i^{\dagger} d_j^{\dagger} d_i d_j + D(S_{3d}^z)^2 \]  

where the indices \( i,j,k,l \) now run over the impurity shell. The one-body part \( h_{ij}^{3d} \) is given by the KS Hamiltonian \( H^D_0 \) projected onto the 3\( d \)-shell with a double-counting correction (DCC), \( h_{ij}^{3d} = (H^D_0)_{ij} - V_{ij}^{\text{DCC}} \). The latter accounts for the fact that Coulomb interaction within the 3\( d \)-shell has already been taken into account in the KS Hamiltonian in an effective mean-field way. Unfortunately, the DCC term \( V_{ij}^{\text{DCC}} \) is not exactly known for DFT, and several approximation schemes are used in practice [47]. Here the so-called atomic limit or fully localized limit (FLL) is employed [48].

Also note that the effective Coulomb interaction \( U_{ij} \) is different from the bare one \( V_{ij} \) due to screening by electron-hole pairs in the rest of the system. It is in principle possible to calculate the screened Coulomb interaction \( U_{ij} \) [32] for example within the constrained random phase approximation [49]. Instead here we make a reasonable guess for the Coulomb matrix elements which leads to good agreement between the calculated STM spectra and the experimental ones (see below). Finally, the last term in (11) yields a phenomenological description of the single-ion magnetic anisotropy (MA) arising from crystal-field splitting of the impurity levels in combination with spin–orbit coupling. As was shown in previous work [15, 25, 26] the MA term gives rise to inelastic spin-flip excitations in the spectral function of the impurity shell.

The coupling between the impurity shell and the rest of the system (i.e. the bath) consisting of the the substrate and the rest of the molecule is described by the embedding self-energy of the 3\( d \)-shell, usually called hybridization function (matrix) and denoted by \( \Delta(\omega) \) in the context of the AIM. The hybridization function matrix of the 3\( d \)-shell can be obtained by reverse engineering from the projection of the device GF onto the 3\( d \)-subspace, \( G_{3d} = P_{3d} G^D_{\text{ks}} P_{3d} \), as

\[ \Delta_{3d}(\omega) = \omega - H^D_{3d} - [G_{3d}(\omega)]^{-1} \]  

where \( H^D_{3d} \) is the KS Hamiltonian projected onto the 3\( d \)-shell.

The impurity Hamiltonian (11) together with the hybridization function (12) completely defines the AIM. Here as in previous works [29, 31, 32, 50] we make use of the so-called one-crossing approximation (OCA) for solving the AIM [51–53]. OCA consists in a diagrammatic expansion of the propagators \( G_\alpha(\omega) \) associated with the many-body eigenstates \( |\alpha\rangle \) of the isolated impurity Hamiltonian (11) in terms of the hybridization function \( \Delta_{3d}(\omega) \), summing only a subset of diagrams (only those where conduction electron lines cross at most once) to infinite order. Once the impurity problem is solved, the many-body spectral function of the impurity shell \( A_{3d}(\omega) \) and the many-body self-energy \( \Sigma_{3d}(\omega) \) describing the interaction effects within the 3\( d \)-shell are obtained. The correlated GF of the central region C is then given by

\[ G_C(\omega) = \left(\omega - H_C^0 - \Sigma^C_C(\omega) - \Sigma^S_S(\omega)\right)^{-1} \]  

where \( \Sigma^C_C(\omega) \) is the many-body self-energy, describing interaction effects within the C region, \( \Sigma^S_S(\omega) \) comprises the static mean-field like Hxc term \( V_{\text{Hxc}} \) of the DFT calculation and the dynamic many-body correction \( \Sigma_{3d}(\omega) - V_{\text{DCC}} \) for the correlated 3\( d \)-subspace: \( \Sigma_{3d}(\omega) = V_{\text{Hxc}} + \Sigma_{3d}(\omega) - V_{\text{DCC}} \). From the GF \( G_C(\omega) \), the spectral function \( A_C(\omega) = -\text{Im} G_C(\omega) \), and thus the STM spectrum of the molecule, taking into account
FeTPPS molecule on the Au(111) surface was relaxed using the molecule on Au(111) substrate probed by STM tip. First the full FeTPPS molecule on the Au(111) surface was relaxed using the VASP code. The four phenyl sulfonyl hydroxide groups were then replaced by hydrogen atoms. See text for further explanations.

Dynamic correlation effects in the 3d-shell of the TM center, can be calculated via (8).

3. Results

3.1. Spin flip excitations of FeP on Au(111)

We now apply the above developed methodology to the description of spin excitations measured recently by STS of an Fe tetraphenylporphyrin sulfonate (FeTPPS) molecule on the Au(111) surface [28]. Similar Fe porphyrin type molecules have recently been measured by other groups [20, 41].

Our starting point is the structure of the full FeTPPS molecule on the Au(111) surface, which was relaxed in previous work using the VASP code with the Perdew, Burke and Ernzerhof (PBE) functional in connection with the van der Waals correction due to Grimme [28]. As can be seen in figure 2 (which shows the truncated FeP molecule, see caption and the discussion below), the porphyrin ring is strongly distorted from a planar geometry due to the binding of the phenyl sulfonate end groups to the Au substrate, similar to the case of manganese tetraphenylporphyrin sulfonate (MnTPPS) on Au(111) [18]. In the next step we perform ab initio DFT calculations as described above, on a simplified system consisting of an iron porphyrin (FeP) molecule on the Au(111) substrate and an STM made of a small [111] pyramid of Au atoms 10 Å above the surface, as depicted in figure 2. The structure of the FeP molecule is that of the larger FeTPPS molecule on Au(111), but with the phenyl sulfonate groups substituted by hydrogen atoms. Hence the local environment of the Fe atom, which determines the crystal field splittings of the 3d-orbitals of the Fe center and their hybridization with the substrate and porphyrin ring, is the same as that of the full FeTPPS molecule.

Previous spin-polarized DFT calculations indicate that the molecule is in a spin-1 ground state [28]. The molecular spin \( S = 1 \) is essentially localized in the 3d-shell of the Fe center, namely in the \( z^2 \) and \( dxz \)-orbitals. The \( xy \)-orbital is completely full and thus does not carry a spin. The spin in the half-filled \( x^2 - y^2 \)-orbital, on the other hand, is completely quenched by strong coupling to the porphyrin ring, similar to the case of manganese porphyrin (MnP) on Au(111) [18].

Spin-polarized DFT calculations predict the ground state of the FeP molecule to be dominated by a single electronic configuration where the symmetry of the two \( dx^2 \)-orbitals is completely broken due to the saddle-like distortion of the porphyrin ring. The spin-1 is thus almost entirely carried by the \( z^2 \) and \( yz \)-orbitals, while the \( xz \)-orbital is essentially full [20]. However, it is well known that this static mean-field picture is not really correct for FeP in the gas phase. Instead a dynamic picture where several electronic configurations close-by in energy, characterized by different occupations of the Fe 3d-shell, contribute significantly to the ground state of the molecule, is more appropriate. Such a dynamic picture of the ground state of FeP derivatives is for example of fundamental importance for understanding the biologically important imbalance between carbon dioxide and carbon monoxide binding to the heme protein [54].

As described above in section 2.3 here we make use of a dynamic treatment of the Fe 3d-shell in terms of an AIM which is solved within the one-crossing approximation. This approach takes into account dynamic fluctuations between different electronic configurations of the 3d-shell. Some of the model parameters of the AIM (impurity level energies and hybridization function) are obtained from the DFT calculation. In order to not artificially spin-polarize the porphyrin ring and metal substrate, we start from a non-magnetic DFT calculation. Here we have employed the generalized gradient approximation (GGA) in the parametrization due to PBE [55] in combination with the LanL2MB basis set plus pseudo potential including the outer core and valence electrons [56]. Figure 3(a) shows the imaginary part of the hybridization potential including the outer core and valence electrons [56]. Table 1 shows the occupancies of the Fe 3d-orbitals for a spin-polarized as well as a non-magnetic DFT calculation. The spin-polarized calculation yields a spin-1 basically localized in the half-filled \( dx^2 \)-orbitals with a small contribution of the \( z^2 \)-orbital. On the other hand, the non-magnetic solution yields an intermediate valence picture for the three orbitals \( z^2, xz \) and \( yz \), indicating fluctuations between configurations with different occupations of these orbitals, which in the spin-polarized DFT calculation is frozen to the lowest energy configuration. Neither the \( x^2 - y^2 \)-orbital nor the \( xy \)-orbital carries a net spin in the spin-polarized DFT calculation. While the latter orbital is basically completely full, the former is actually half-filled. However, the spin in the \( x^2 - y^2 \)-orbital is completely quenched due to the strong coupling of this orbital to the porphyrin ring, indicated by the two strong resonances in the broadening (yellow line in figure 3(a)) around \( \omega \sim -0.5 \) eV and \( \omega \sim -0.8 \) eV. This orbital has the strongest hybridization of all Fe 3d-orbitals (note the logarithmic scale). In contrast the fully occupied \( xy \)-orbital has the weakest hybridization of all 3d-orbitals, as it basically does couple to the substrate or porphyrin ring.
Au(1 1 1) due to coupling to (a) the rest of the molecule and surface levels. 

Figure 3. Broadening of Fe 3d-orbitals of FeP molecule on Au(1 1 1) due to coupling to (a) the rest of the molecule and surface (Γ_{3d}) and (b) to the STM tip placed at 10 Å above the substrate (Γ_{T}). Γ_{3d} is given by the imaginary part of the hybridization function, Γ_{3d} = −2ImΔ_{3d}, while Γ_{T} is given by the imaginary part the embedding self-energy for the tip electrode, Γ_{T} = −2ImΣ_{T}, which can be obtained from equation (10).

Table 1. Orbital-resolved occupation numbers of Fe 3d-shell for spin-polarized GGA (SP-GGA, occupations per spin), non-magnetic GGA (NM-GGA), and OCA calculations of the 3AIM for different shifts δε (given in parentheses) of the impurity energy levels.

| Calc.     | z²   | xz   | yz   | x² − y² | xy   |
|-----------|------|------|------|---------|------|
| SP-GGA (+) | 0.96 | 0.98 | 0.98 | 0.61    | 1.00 |
| SP-GGA (−) | 0.77 | 0.21 | 0.23 | 0.52    | 0.99 |
| NM-GGA    | 1.50 | 1.49 | 1.34 | 1.06    | 1.99 |
| OCA (−0.5eV) | 1.92 | 1.14 | 1.19 | —       | —    |
| OCA (+0.0eV) | 1.90 | 1.11 | 1.15 | —       | —    |
| OCA (+0.5eV) | 1.86 | 1.09 | 1.13 | —       | —    |

Hence it is clear that the spin is localized in the z²- and d₅ₛ-orbitals of the Fe center, and that fluctuations between different electronic configurations of the FeP molecule chiefly concern these three orbitals. This justifies the use of a three-orbital AIM to model the dynamics of the Fe center coupled to the porphyrin ring and Au surface, consisting of the z²-, xz- and yz-orbitals only. The broadening of the z²-orbital has a relatively smooth energy dependence around the Fermi level as it mainly couples to the s-type conduction electrons of the Au substrate. On the other hand, for symmetry reasons the xz- and yz-orbitals do not couple to the s-type conduction electrons in the substrate at all, but show significant coupling to molecular orbitals of the porphyrin ring indicated by the pronounced resonances in the hybridization function of these two orbitals.

Figure 3(b) shows the broadening of the Fe 3d-orbitals due to the coupling to the STM tip 10 Å above the surface, computed from the non-magnetic DFT solution via equation (10). Comparison with figure 3(a) shows that the tip coupling is smaller by several orders of magnitude than the coupling to the substrate and the porphyrin ring, thus justifying the assumption Γ_{T} ≪ Γ_{S} made in deriving (8). Importantly, the tip broadening around the Fermi level for the z²-orbital is larger than that of the other orbitals by at least one order of magnitude, as only this orbital couples to the s-type conduction electrons in the tip due to symmetry reasons.

Next the three-orbital AIM consisting of the z²-, xz- and yz-orbitals coupled to the Au substrate and porphyrin ring is solved using the one-crossing approximation, for the hybridization function, shown in figure 3(a), and impurity levels extracted from the non-magnetic DFT calculation as described above. For the interaction parameters we use U = 5.3 eV for the intra-orbital Coulomb repulsion (U_{ii}), U' = 3.9 eV for the inter-orbital Coulomb repulsion (U_{ij} with i ≠ j) and J_{H} = 0.7 eV for the Hund’s rule coupling (U_{ij} with i ≠ j). The uni-axial magnetic anisotropy is set to D = 10 meV. We have checked that changing the parameters within reasonable bounds does not alter the results in an essential way.

In figures 4(a)–(c) the many-body spectral functions of the impurity orbitals calculated within OCA at low temperature (T ∼ 10 K) are shown. As the DCC is not exactly known (see above) we have also explored the effect of shifting the impurity levels in energy by ±0.5 eV w.r.t. the value obtained using the FLL DCC. The spectra of all three orbitals show the typical step features associated with spin-flip excitations of a spin-1 magnetic quantum. It is interesting that even though the spin S ∼ 1 is mainly localized in the half-filled xz- and yz-orbitals, with only a minor contribution coming from the nearly full z²-orbital (see table 1), the spin flip excitation steps are clearly visible in the spectra of all three orbitals.

The excitation energies are renormalized to about Δ₅ ≈ ±8 meV w.r.t. the bare value of Δ₅ = ±D = ±10 meV due to exchange coupling to the conduction electrons in the Au substrate and porphyrin ring [15, 25, 26]. The value for the uni-axial MA of D = 10 meV has of course been chosen such as to reproduce the experimentally observed spin flip excitation energies for the FeTPPS molecule on the Au(1 1 1) substrate [28]. This value is also in good agreement with the ones measured for similar iron porphyrin systems on the same substrate [20, 41].

As the impurity level energies are shifted, the spectra of the three orbitals behave quite differently: while the amplitude of the spin excitations of the xz- and yz-orbitals increases when the impurity levels are lowered in energy, the z²-orbital shows just the opposite behavior. This can be understood by considering the charge fluctuations (measured as the deviation from integer occupancy) of individual orbitals as a function of the energy shift (see table 1): while the charge fluctuations...
of the nearly half-filled (singly occupied) $x\sigma_+$ and $y\sigma_-$ orbitals increase, the charge fluctuations of the nearly filled (doubly occupied) $z^2$-orbital decrease, when the impurity levels are lowered in energy. As was shown in previous work [26], the amplitudes of the spectral features associated with the spin-flip excitations increase (decrease) as the charge fluctuations in the corresponding orbitals increase (decrease). Simultaneously, the asymmetry of the spectra increases (decreases) with increasing (decreasing) charge fluctuations.

Finally, figure 4(d) shows the $dI/dV$-spectra calculated from the spectral function of the C region according to (8). The STM spectra are dominated by the spectral function of the $z^2$-orbital plus a linear background stemming from tunneling through the rest of the molecule. The spectral functions of the $xz$- and $yz$-orbitals only contribute indirectly (via coupling to orbitals on neighboring atoms in the molecule) to the $dI/dV$ spectra, since their coupling to the STM tip is suppressed by one order of magnitude compared to that of the $z^2$-orbital, as discussed above. The resemblance of the calculated $dI/dV$ spectrum with the experimentally measured ones for different iron porphyrin type molecules on the Au surface is quite remarkable [20, 28, 41]. In contrast the amplitudes of the spectral features associated with the spin-flip excitations increase (decrease) as the charge fluctuations in the corresponding orbitals increase (decrease). Simultaneously, the asymmetry of the spectra increases (decreases) with increasing (decreasing) charge fluctuations.

The theoretical results suggest that the relatively small differences in the experimental spectra of different FeP type molecules [20, 28, 41] may to some degree be attributed to small variations in the occupancy of the Fe 3$d$-orbitals, which in turn lead to variations in the spectral functions according to figure 4. The main difference between the experimental and theoretical spectra calculated in the ideal STM limit from equation (8) seems to lie in the background dispersion which may be attributed to the use of an incomplete basis set and approximate functionals in the DFT calculations. However, also quantum interference effects in the tunneling between the tip and molecule, not taken into account in (8), may play a minor role in determining the actual lineshapes of the spin-flip excitations in the STM spectra.

### 3.2. Kondo effect of Mn porphyrin on Au(1 1 1)

Naturally, also the Kondo effect, which can be seen as a zero-energy or elastic spin flip excitation, can be described within this approach. Let us thus briefly revisit the case of a Mn tetraphenylporphyrin sulfonate (MnTPPS) molecule on the Au(1 1 1) substrate. There the STM spectra showed a zero-bias anomaly, which was explained as due to an under-screened Kondo effect in the $z^2$-orbital strongly enhanced by charge fluctuations [18]. The main difference with the Fe case, considered in the previous section, is that for Mn the molecule is close to a spin-3/2 state. Thus assuming a positive MA ($D > 0$) the ground state is the $S = 3/2, S_z = \pm 1/2$ doublet, which can give rise to the Kondo effect in contrast to the non-degenerate $S = 1, S_z = 0$ ground state in the Fe case. Additionally, part of the spin is now localized in the $z^2$-orbital.
which couples strongly to the substrate and experiences stong charge fluctuations, leading to a relatively broad Kondo resonance in the $z^2$-orbital and additionally to a strong renormalization of the effective MA $[15,26]$. As the $z^2$-orbital is also the orbital that most strongly couples to the $s$-type conduction electrons of the STM tip, the broad Kondo resonance would be the only feature visible in the STM spectrum, even if inelastic steps due to MA appear in the other less strongly coupled $d$-orbitals of the Mn center.

We now calculate the $dI/dV$ spectrum using (8) for the truncated MnP molecule on Au(1 1 1), also considered in our previous work. Similar to the truncated FeP molecule considered above, first the full MnTPPS molecule on the Au(1 1 1) substrate was relaxed with the VASP code (see supplemental material of [18] for more details). Then ab initio DFT calculations using the PBE functional plus Lanl2MB basis set plus pseudo potentials are performed on a truncated molecule with the four phenyl sulfonate groups replaced by hydrogen atoms. The Anderson model consisting of the Mn 3d-shell coupled to the rest of the system (porphyrin ring plus Au substrate) is solved within the OCA which yields the spectral functions and many-body self-energies of the Mn 3d-orbitals.

Finally, the $dI/dV$ spectra are calculated according to (8) for the STM tip at 10 Å above the surface. The results are shown in figure 5 for different shifts $\delta\epsilon$ of the impurity level energies w.r.t. the value given by the FLL DCC. The $dI/dV$ shows a Kondo resonance close to zero bias, stemming from the underscreened Kondo effect in the Mn $z^2$-orbital. For the impurity level energies given exactly by the FLL DCC, the charge fluctuations lead to a relatively broad and somewhat asymmetric Kondo resonance. As the impurity levels are shifted upwards in energy the charge fluctuations decrease and lead to a sharper and more symmetric Kondo resonance. However, the lineshapes in the experimental STM spectra are considerably more asymmetric than the ones calculated in the ideal STM limit (8). In fact, the STM spectra calculated using the phase coherent approximation in our previous work showed a far better agreement with the experimental spectra [18]. For comparison figure 5, also shows the $dI/dV$ calculated in the phase coherent approximation from the correlated transmission function $T(\omega)$ [29,32] which shows rather a Fano-like behavior, not captured by the $dI/dV$ calculated in the ideal STM limit. Apparently, despite the weak coupling to the STM tip and in contrast to the inelastic spin flip excitations, quantum interference in the tunneling processes thus still plays a significant role for determining the actual lineshape of the zero-bias anomaly associated with the Kondo effect.

4. Conclusions

In this work a semi ab initio scheme for calculating the STM spectra of magnetic molecules on metallic substrates has been devised, which takes properly into account many-body effects, leading to inelastic spin flip excitations. The calculated STM spectra of an FeP molecule on the Au(1 1 1) substrate show the typical step features characteristic for inelastic spin flip excitations, and are in good agreement with STM spectra recently measured in several experiments on similar FeP type molecule on Au(1 1 1) [20,28,41]. While part of the mild discrepancies between experimental and theoretical spectra may be attributed to the use of approximate functionals and truncated basis sets in the density functional calculations, also quantum interference effects, explicitly neglected in the ideal STM limit considered here, may play a minor role in the end. In contrast, in the case of Kondo effect quantum interference plays a crucial role in determining the actual lineshape of the zero-bias anomaly in the STM spectra even for very weak coupling to the STM tip. To reconcile the ideal STM limit, properly taking into account inelastic many-body scattering, with the phase coherent approximation, correctly describing quantum interference, is the subject of ongoing research.

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