

Inelastic electron tunneling through adatoms and molecular nanomagnets

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We discuss a theoretical description of the inelastic electron tunneling spectra (IETS) of a magnetic nanosystem (an atom or a molecule) adsorbed on a solid surface measured in a scanning tunneling microscope (STM). We represent the nanosystem by means of a cluster Hubbard model, which allows us to study scenarios when the tunneling electrons sequentially interact with several magnetic centers inside the nanosystem or when the magnetic centers are made out of heavy atoms with a strong spin-orbit coupling and large orbital moments. The sequential tunneling through multiple centers is illustrated on an adatom probed by an STM tip with a nickelocene molecule attached to it. For atoms with large orbital moments, we find that the exchange interaction between the atom and the spin $\mathbf{s}$ of the tunneling electron is richer than the usually assumed Heisenberg form $\mathbf{S} \cdot \mathbf{s}$ or $\mathbf{J} \cdot \mathbf{s}$, where $\mathbf{S}$ and $\mathbf{J}$ are the spin and total orbital moments of the atom. For atoms in axially symmetric environments, the $\mathbf{J} \cdot \mathbf{s}$ exchange would restrict the transitions accessible by IETS to those fulfilling $|\Delta J_z| \leq 1$, where J_z is the projection of the total angular momentum to the symmetry axis, whereas we arrive at a more permissive selection rule $|\Delta J_z| \leq 2\ell + 1$, where ℓ is the orbital momentum quantum number of the partially filled atomic shell carrying the magnetic moment.

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I. INTRODUCTION

The inelastic electron tunneling spectroscopy (IETS) was initially developed for characterization of molecular vibrations, representing a complementary tool to the Raman spectroscopy [1,2]. The observation of electronic transitions (including f - f transitions) followed soon afterward [3–5]. The measurements were originally done on ensembles of molecules placed inside metal-insulator-metal tunnel junctions, but we are concerned with inelastic spectroscopy of a single atom or molecule in a scanning tunneling microscope (STM) [6,7]. Namely, we discuss theoretical description of the spin-excitation spectroscopy [8,9], which is usually modeled in terms of the spin-assisted tunneling Hamiltonians considering an exchange between the spin of the tunneling electron and the spin of the nanosystem adsorbed on the surface [10–13]. We employ an alternative strategy, working directly with electronic instead of spin degrees of freedom, which facilitates a straightforward generalization to scenarios when the tunneling involves sequential interactions of the tunneling electron with several magnetic centers (for instance, when the STM tip has a magnetic molecule attached [14–16]) or when atoms with large orbital moments are among the magnetic centers in the nanosystem. On top of that, the electronic model

enables a unified description of IETS and x-ray magnetic circular dichroism [16].

II. DIFFERENTIAL CONDUCTANCE

We approximate the magnetic nanosystem by the cluster Hubbard model $\hat{\mathcal{H}}_{\text{ns}}$, each magnetic center being represented by one site of the model [17]. The metallic electrodes (tip and surface) are taken as reservoirs of noninteracting electrons (with Hamiltonians $\hat{\mathcal{H}}_t$ and $\hat{\mathcal{H}}_s$). The coupling between the electrodes and the nanosystem is described by a tunneling operator

$$\hat{\mathcal{V}} = \sum_{k i \Gamma \mu} (A_{k i \Gamma} \hat{a}_{k i \Gamma \mu}^\dagger \hat{d}_{i \Gamma \mu} + B_{k i \Gamma} \hat{b}_{k i \Gamma \mu}^\dagger \hat{d}_{i \Gamma \mu} + \text{H.c.}), \quad (1)$$

where the electron operators $\hat{d}$ correspond to the one-electron states defining the magnetic centers, and the operators $\hat{a}$ and $\hat{b}$ correspond to the conduction-electron states in the tip and surface. Index k is a star of a wave vector combined with the band index, i enumerates the magnetic centers, Γ labels irreducible representations at a given magnetic center, and μ labels components of Γ if it is multidimensional. The states $\hat{a}_{k i \Gamma \mu}$ ($\hat{b}_{k i \Gamma \mu}$) are one-electron eigenstates of $\hat{\mathcal{H}}_t$ ($\hat{\mathcal{H}}_s$) with an energy ϵ_k . For a magnetic center surrounded by an isotropic environment, μ would be $m\sigma$, where m and σ are magnetic and spin quantum numbers, and $\hat{a}_{k i \Gamma \mu}$ would be spherical waves around the center i . Defined this way, the operator $\hat{\mathcal{V}}$ conserves the symmetry of the magnetic centers [18–20].

The states $\hat{a}_{k i \Gamma \mu}$ and $\hat{a}_{k' i' \Gamma' \mu'}$ coupled to different centers, $i \neq i'$, are not mutually orthogonal, in general, but we impose this orthogonality as an additional simplification. This simplification does not come into play when each electrode is

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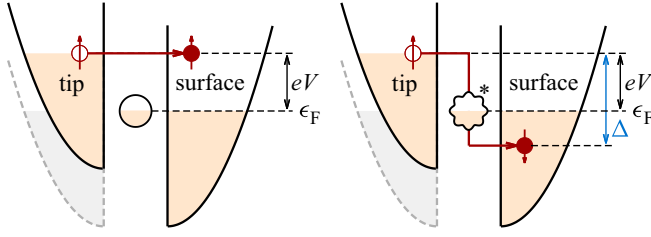


FIG. 1. Elastic (left) and inelastic (right) tunneling. The STM arrangement consists of a tip (left electrode), a surface (right electrode), and a magnetic nanosystem in between. A voltage V is applied to the tip, which lifts its Fermi level up by the energy eV . The inelastic channel is active only when the voltage exceeds the excitation energy Δ of the nanosystem, $eV > \Delta$, otherwise there is no empty final state available.

coupled to only one magnetic center. In addition, we neglect the energy dependence of the tunneling amplitudes $A_{ki\Gamma}$ and $B_{ki\Gamma}$ and replace them with $A_{i\Gamma}$ and $B_{i\Gamma}$. This is reasonable since magnetic IETS typically probes the conduction states in the electrodes only in a small energy window of several tens of meV around the Fermi level ϵ_F , where the energy dependence can be replaced by a constant.

The many-body eigenstates of $\hat{\mathcal{H}}_{\text{ns}}$ are denoted as $|\psi_{N\alpha}\rangle$, where N is the number of electrons in the nanosystem and α indexes the states within the fixed- N subspace of the full Hilbert space. The corresponding energies are $E_{N\alpha}$. To simplify the notation, we introduce a class of many-body eigenstates of the whole system $|\chi_{N\alpha}\rangle = |\phi_t\rangle \otimes |\phi_s\rangle \otimes |\psi_{N\alpha}\rangle$, where $|\phi_s\rangle$ is the ground state of the surface electrode (all states with single-particle energies $\epsilon_k < \epsilon_F$ are filled) and $|\phi_t\rangle$ is the ground state of the tip (all states with single-particle energies $\epsilon_k < \epsilon_F + eV$ are filled, since the tip is at a voltage V above the surface, Fig. 1). The energy of $|\chi_{N\alpha}\rangle$ is $\mathcal{E}_{N\alpha} = E_{N\alpha} + E_t + E_s$, where E_t and E_s are the ground-state energies of the tip and surface.

Starting from the initial state $|\chi_{N\alpha}\rangle$, the tunneling from the tip to the surface proceeds along one of two paths: (1) an electron jumps from the tip to the nanosystem and then the same (or another) electron jumps from the nanosystem to the surface or (2) an electron jumps from the nanosystem to the surface and then an electron from the tip fills the hole created in the nanosystem. In the first case, there is a (virtual) intermediate state $|v\rangle$ with $N + 1$ electrons in the nanosystem and with energy $\mathcal{E}_v$. In the second case, the intermediate state has $N - 1$ electrons in the nanosystem. Such coherent two-step processes are known as cotunneling [21,22]. There exist tunneling paths involving virtual states with $N \pm n$ electrons in the nanosystem, where $n > 1$, that correspond to higher orders of the expansion in the tunneling operator $\hat{\mathcal{V}}$. We assume that the tunneling amplitudes $A_{ki\Gamma}$ and $B_{ki\Gamma}$ are small compared to the charging energy of the nanosystem $U \sim E_{N\pm 1, \alpha} - E_{N\alpha}$ (Coulomb blockade regime) and that the higher-order processes can be neglected. The assumption of the higher-order terms being negligible is stronger than the assumption of small amplitudes $A_{ki\Gamma}$ and $B_{ki\Gamma}$ as nonperturbative higher-order effects, like Kondo, can appear no matter how small the tunneling amplitudes are. Such effects are out of reach of the theory we discuss in this paper.

We consider the tunneling as a series of independent events, which is a good approximation as long as the tunneling current is low and the nanosystem has enough time to decay from an excited final state before the next tunneling event starts. We also neglect all temperature effects so the tunneling always starts from the ground state of the nanosystem and electrodes. Under these assumptions, the tunneling current can be calculated from the Kramers–Heisenberg formula [23,24] that is routinely used in simulations of another type of inelastic spectroscopy, the resonant inelastic x-ray scattering [25,26]. In the present context, the formula reads

$$I_{\pm} \sim \pm \sum_{f_{\pm}} \left| \sum_v \frac{\langle f_{\pm} | \hat{\mathcal{V}} | v \rangle \langle v | \hat{\mathcal{V}} | \chi_{N\alpha} \rangle}{\mathcal{E}_v - \mathcal{E}_{N\alpha}} \right|^2 \delta(\mathcal{E}_{f_{\pm}} - \mathcal{E}_{N\alpha}), \quad (2)$$

where the positive current I_+ comes from the final states $|f_+\rangle = \hat{b}_{k'i'\Gamma'\mu'}^\dagger \hat{a}_{ki\Gamma\mu} |\chi_{N\beta}\rangle$ with $\epsilon_k < \epsilon_F + eV$ and $\epsilon_{k'} > \epsilon_F$, and the negative current I_- comes from the final states $|f_-\rangle = \hat{a}_{ki\Gamma\mu}^\dagger \hat{b}_{k'i'\Gamma'\mu'} |\chi_{N\beta}\rangle$ with $\epsilon_k > \epsilon_F + eV$ and $\epsilon_{k'} < \epsilon_F$. The final-state energies are $\mathcal{E}_{f_{\pm}} = \mathcal{E}_{N\beta} \mp \epsilon_k \pm \epsilon_{k'}$. Index α corresponds to the ground state of the nanosystem, the final states with $\beta \neq \alpha$ indicate inelastic channels. If the ground state is degenerate, the current is computed as an average over the degenerate ground states.

Fixing the nanosystem at the same voltage as the surface (Fig. 1), which also implies neglecting any voltage gradient within the nanosystem, and integrating out the degrees of freedom of the electrodes, we arrive at a formula for the differential conductance,

$$\frac{dI}{dV} = \sum_{\substack{\beta \\ \Delta_{\beta\alpha} < eV}} \mathcal{G}_{\alpha\beta} + \sum_{\substack{\beta \\ \Delta_{\beta\alpha} < -eV}} \mathcal{G}_{\beta\alpha}, \quad (3a)$$

where $\Delta_{\beta\alpha} = E_{N\beta} - E_{N\alpha} > 0$. The first term contributes only at positive biases V (giving positive current), the second term contributes only at negative V (giving negative current). As the bias voltage increases, progressively more terms contribute to the sums (states with larger $\Delta_{\beta\alpha}$ can be excited), which produces steps in dI/dV and peaks in d^2I/dV^2 spectra.

The partial conductances $\mathcal{G}_{\alpha\beta}$ have the form

$$\mathcal{G}_{\alpha\beta} = \frac{2\pi e^2}{\hbar} \sum_{i'i'\Gamma'\mu'} |A_{i\Gamma} B_{i'\Gamma'}|^2 \rho_{i\Gamma}^t(eV) \rho_{i'\Gamma'}^s(eV - \Delta_{\beta\alpha}) \times |\langle \psi_{N\beta} | \hat{\mathcal{O}}_{i\Gamma\mu}^{\alpha\beta} | \psi_{N\alpha} \rangle|^2, \quad (3b)$$

where $\rho_{i\Gamma}^t$ is the density of states (DOS) in the tip projected onto orbitals $\hat{a}_{i\Gamma\mu}$ and $\rho_{i'\Gamma'}^s$ is the analogous DOS in the surface projected onto orbitals $\hat{b}_{i'\Gamma'\mu'}$. Neither of these DOSs depends on μ as dictated by symmetry. Further on, we neglect the energy dependence of the DOSs analogously as we do for the amplitudes $A_{i\Gamma}$ and $B_{i\Gamma}$. Finally, the transition operator entering Eq. (3b),

$$\hat{\mathcal{O}}_{i\Gamma\mu}^{\alpha\beta} = \hat{d}_{i'\Gamma'\mu'} \frac{1}{\hat{\mathcal{H}}_{\text{ns}} - E_{N\alpha} - eV} \hat{d}_{i\Gamma\mu}^\dagger - \hat{d}_{i\Gamma\mu}^\dagger \frac{1}{\hat{\mathcal{H}}_{\text{ns}} - E_{N\beta} + eV} \hat{d}_{i'\Gamma'\mu'}, \quad (3c)$$

determines the intensities of the inelastic transitions and their selection rules. The two terms in Eq. (3c) are the two

cotunneling paths. The matrix elements of $\hat{O}_{i\Gamma\mu i\Gamma'\mu'}^{\alpha\beta}$ in Eq. (3b) scale as $1/U$, since the denominators always contain a difference like $E_{N\pm 1,\beta} - E_{N\alpha} \sim U$ and eV is small compared to U (several eV for U versus less than 0.1 eV for eV , typically). Consequently, the conductances $\mathcal{G}_{\alpha\beta}$ scale as $|A_{i\Gamma}B_{i\Gamma'}|^2/U^2$. Details of the derivation of Eqs. (3) are given in Ref. [27].

The evaluation of the matrix elements of $\hat{O}_{i\Gamma\mu i\Gamma'\mu'}^{\alpha\beta}$ is a many-body problem that we solve numerically by means of Krylov-subspace methods. The low-lying eigenstates of the nanosystem $|\psi_{N\beta}\rangle$ are found using the implicitly restarted Lanczos method [28], the matrix elements themselves are computed using the band Lanczos method [29,30].

Our description of IETS is essentially the same as the low-current and zero-temperature limit of the theory formulated in Ref. [31].¹ Only the tunneling operator from Ref. [31], with terms like $\hat{a}_{k\sigma}^\dagger \hat{d}_{im\sigma}$ that couple the magnetic centers to the Bloch waves $\hat{a}_{k\sigma}$ instead of the symmetry-adapted waves $\hat{a}_{ki\Gamma\mu}$, differs from our tunneling operator, Eq. (1). This leads to a modification of Eq. (3b); the sums over the orbital degrees of freedom (i and m) are inside the modulus squared, whereas the sums over the spin σ stay outside like in our result. Such an alternative expression for the differential conductance has a spurious symmetry breaking built in as we illustrate in Ref. [27].

III. THE NANOSYSTEM

The applications discussed below fit into a framework of $\hat{\mathcal{H}}_{\text{ns}} = \sum_i \hat{\mathcal{H}}_i + \sum_{i<j} \hat{\mathcal{T}}_{ij} + \sum_i \hat{\mathcal{U}}_i$, where $\hat{\mathcal{H}}_i$ characterizes an individual magnetic center (a partially filled atomic shell with orbital momentum quantum number ℓ_i), $\hat{\mathcal{T}}_{ij}$ describes hopping of electrons between two shells, and $\hat{\mathcal{U}}_i$ is the Coulomb repulsion within a shell. Each shell

$$\hat{\mathcal{H}}_i = \sum_{\substack{mm' \\ \sigma\sigma'}} ([\zeta^i \boldsymbol{\ell} \cdot \mathbf{s} - \boldsymbol{\mu} \cdot \mathbf{B}]_{mm'}^{\sigma\sigma'} + h_{mm'}^i \delta_{\sigma\sigma'}) \hat{d}_{im\sigma}^\dagger \hat{d}_{im'\sigma'} \quad (4)$$

contains the spin-orbit coupling specified by its strength ζ^i , the interaction of the magnetic moment $\boldsymbol{\mu} = \mu_B(\boldsymbol{\ell} + 2\mathbf{s})$ with a magnetic field $\mathbf{B}$, and the crystal-field potential h^i that we define using the Wybourne parameters B_{kq}^i . The energy of the atomic level ϵ^i is included in h^i as the $(k, q) = (0, 0)$ term with $B_{00}^i = \epsilon^i$. The hopping operator $\hat{\mathcal{T}}_{ij}$ has the form

$$\hat{\mathcal{T}}_{ij} = \sum_{\sigma mm'} (t_{mm'}^{ij} \hat{d}_{im\sigma}^\dagger \hat{d}_{jm'\sigma} + \text{H.c.}), \quad (5)$$

that is, the electron spin is conserved when the electron hops from one magnetic center to another. The Coulomb interaction $\hat{\mathcal{U}}_i$ could include crystal-field effects [32,33], but we assume a spherically symmetric operator characterized by Slater parameters F_k^i , $k = 0, 2, \dots, 2\ell_i$ [34]. The Coulomb interaction could also act between shells, especially if they are located at the same atom [35], but we leave such settings out for now.

¹Equation (2) is the same as the Fermi golden rule $I_{\pm} = \pm(2\pi e/\hbar) \sum_{f_{\pm}} |\mathcal{H}_{\text{cotun}}|^2 \delta(\mathcal{E}_{f_{\pm}} - \mathcal{E}_{N\alpha})$ if the cotunneling Hamiltonian $\mathcal{H}_{\text{cotun}} = \sum_v (f_{\pm} |\hat{v}\rangle \langle v| \hat{V} | \chi_{N\alpha}) / (\mathcal{E}_v - \mathcal{E}_{N\alpha})$ is introduced as in Ref. [31].

The hopping amplitudes $t_{mm'}^{ij}$, connecting the individual magnetic centers, can be arbitrarily large since they are treated nonperturbatively together with the rest of the nanosystem Hamiltonian $\hat{\mathcal{H}}_{\text{ns}}$. They should not be confused with the tunneling amplitudes $A_{ki\Gamma}$ and $B_{ki\Gamma}$, entering Eq. (1), which have to be small in comparison to the charging energy of the nanosystem $U \sim \min_i \hat{\mathcal{U}}_i$, since $|A_{ki\Gamma}|^2/U$ and $|B_{ki\Gamma}|^2/U$ act as the small parameters controlling our perturbation theory. To prevent any such confusion, we systematically use *tunneling* for the electron transfer between the nanosystem and electrodes and *hopping* for the electron transfer within the nanosystem.

A realistic nanosystem will typically have more degrees of freedom than just those included in our Hamiltonian $\hat{\mathcal{H}}_{\text{ns}}$. In particular, there will also be empty outer atomic shells, providing additional pathways for the tunneling current. As long as these degrees of freedom do not couple to the magnetic centers, the tunneling current associated with them does not induce any magnetic excitations and they are therefore irrelevant for our discussion of the inelastic spectra. But it is to be expected that the *elastic* conductance computed from Eqs. (3) with our $\hat{\mathcal{H}}_{\text{ns}}$ is incomplete and underestimates the elastic conductance that would be measured in an actual experiment.

IV. NICKELOCENE-TERMINATED STM TIP ABOVE AN IRON ADATOM

We revisit the inelastic tunneling spectra of an iron adatom on the Cu(100) surface measured with an STM tip having a nickelocene (Nc) molecule attached to it [15]. The nickel atom in nickelocene has eight electrons in its $3d$ shell carrying spin $S_{\text{Ni}} = 1$. It has a fivefold symmetry, thus only the axial anisotropy parameter D_{Ni} of the anisotropic spin model can be nonzero, splitting the spin triplet into a singlet, $S_{z,\text{Ni}} = 0$ (the ground state), and a doublet, $S_{z,\text{Ni}} = \pm 1$. The magnitude of D_{Ni} , which gives the gap between the singlet and the doublet, slightly depends on the environment around the Nc molecule, being between 3.2 and 4.0 meV [14–16,37]. The motivation for attaching nickelocene to the STM tip is analogous to magnetometry applications of the nitrogen-vacancy centers in diamond [38,39]: a magnetic field or an exchange field generated by nearby magnetic moments splits the $S_{z,\text{Ni}} = \pm 1$ doublet and, when detected, this splitting provides information about the field.

The Fe atom adsorbed at the hollow site of the Cu(100) surface carries spin $S_{\text{Fe}} = 3/2$ as found in density functional theory (DFT) calculations [15,27,40]. The site has C_{4v} symmetry which again allows only the axial anisotropy D_{Fe} to be nonzero. The model of the coupled Ni and Fe spins reads

$$\hat{\mathcal{H}}_{\text{spin}} = D_{\text{Ni}} \hat{S}_{z,\text{Ni}}^2 + D_{\text{Fe}} \hat{S}_{z,\text{Fe}}^2 - J \hat{\mathbf{S}}_{\text{Ni}} \cdot \hat{\mathbf{S}}_{\text{Fe}} \quad (6)$$

when the isotropic Heisenberg exchange J is assumed. In the setup of Verlhac *et al.* [15], the Nc molecule is oriented such that its z axis is (nearly) perpendicular to the Cu surface. The measured d^2I/dV^2 spectra show the Nc excitation at 3.5 meV, the splitting of which increases as the STM tip approaches the surface and the Ni–Fe distance decreases, and no other excitations are detected up to 10 mV of applied voltage. The observations are well reproduced by assuming the Fe atom to have a large out-of-plane anisotropy, which

TABLE I. Parameters of the atomic shells constituting our nanosystems $\hat{\mathcal{H}}_{\text{ns}}$, and the axial anisotropy parameter D of the spin models corresponding to these shells. Rows A and B are used in Fig. 2, rows A, C, and D in Figs. 5–7, rows E and F in Fig. 3, and row G in Fig. 4. The origin of the parameters of the $3d$ shells is discussed in the text; the parameters of the f shells are taken from Ref. [36] (U^{3+} ion). The magnetic field B_z in the f shells is chosen such that the Zeeman-level spacing comes out as 1 meV.

Ion	Configuration	D (meV)	ζ (meV)	$\epsilon = B_{00}$ (eV)	B_{20} (eV)	B_{40} (eV)	B_{44} (eV)	B_z (T)	B_z^{xc} (T)	F_0 (eV)	F_2 (eV)	F_4 (eV)	F_6 (eV)
A	Ni^{2+} $(x^2 - y^2, xy)^4(z^2)^2(xz, yz)^2$	3.5	82.6	−58.6	3.400	−8.160				8.0	9.786	6.078	
B	Fe^+ $(xy)^2(xz, yz)^3(z^2)^1(x^2 - y^2)^1$	−7.5	45.4	−50.6	0.140	0.646	−1.762			8.0	7.809	4.814	
C	Fe^+ $(xy)^2(x^2 - y^2)^2(xz, yz)^2(z^2)^1$	−7.5	45.4	−50.6	7.840	2.184	0.000			8.0	7.809	4.814	
D	Fe^+ $(xy)^2(x^2 - y^2)^2(xz, yz)^2(z^2)^1$	−0.5	45.4	−50.6	4.700	−1.200	0.000			8.0	7.809	4.814	
E	f^7		235	−17.95				8.80		3.0	7.09	4.60	3.36
F	f^{11}		235	−29.90				14.48		3.0	7.09	4.60	3.36
G	d^8 $(xz, yz)^4(z^2)^1(x^2 - y^2, xy)^3$		82.6	−58.0	−2.000	3.750		40	70	8.0	9.786	6.078	

effectively freezes the Fe spin to the $S_{z,\text{Fe}} = \pm 3/2$ state in the whole voltage range explored in the experiment. The two-spin model, Eq. (6), then simplifies to a model for the Ni spin alone, with the exchange converted to a Zeeman-like term $\Delta_z^{\text{xc}} \hat{S}_{z,\text{Ni}}$ with $\Delta_z^{\text{xc}} = 3J/2$. As discussed in Ref. [15], the d^2I/dV^2 spectra can be estimated by methods reviewed in Ref. [13] and their shape is controlled by two independent parameters: The exchange field Δ_z^{xc} gives the splitting of the $S_{z,\text{Ni}} = \pm 1$ level, and the polarization of the surface electrode due to the frozen out-of-plane Fe spin causes the asymmetry of the spectra with respect to the voltage polarity [41].

To apply our electronic model, we need to estimate the parameters entering $\hat{\mathcal{H}}_{\text{ns}}$. Ideally, they would be determined from first principles [42,43], but we opt for a simpler heuristic approach. The spin-orbit parameter ζ and the Slater parameters F_k are taken from Hartree–Fock calculations [44] of Ni^{2+} ion ($3d^8 4s^0$ configuration) and Fe^+ ion ($3d^7 4s^0$ configuration). The parameters F_k are additionally scaled by a factor 0.8 to mimic screening by the environment. The crystal-field parameters B_{kq} are set such that the individual orbitals in the ground state of $\hat{\mathcal{H}}_{\text{ns}}$ are filled like in the DFT ground state and the resulting spin anisotropy is consistent with experiments. The Ni $3d$ shell in nickelocene has configuration $(x^2 - y^2, xy)^4(z^2)^2(xz, yz)^2$ [45], and the anisotropy is $D_{\text{Ni}} = 3.5$ meV. The $3d$ shell in Fe adatom has configuration $(xy)^2(xz, yz)^3(z^2)^1(x^2 - y^2)^1$ [27], and the anisotropy D_{Fe} is negative and larger than 5 meV, so the first crystal-field excitation lies above 10 meV (we use $D_{\text{Fe}} = -7.5$ meV). This procedure does not specify B_{kq} uniquely, hence our calculations are not the definite solution of the Fe adatom on Cu(100), rather, they represent a proof of concept. The hopping $\hat{T}_{ij}$, Eq. (5), is taken in a simple form with $t_{mm'} = t\delta_{mm'}$ where t is a monotonous decreasing function of the distance between the Nc molecule and the Fe adatom. With such $\hat{T}_{ij}$, the spin σ and the magnetic quantum number m are conserved when electrons hop between the shells. All parameters of $\hat{\mathcal{H}}_{\text{ns}}$ are summarized in Table I.

The left panel of Fig. 2 compares the lowest excitations of $\hat{\mathcal{H}}_{\text{ns}}$ to the spectrum of the spin model, Eq. (6), when the appropriate relation between the hopping t and the exchange J , $J \sim t^2/U$, is utilized. The excitations around 3.5 meV, corresponding to a change of the Ni spin direction, match perfectly. The higher excitations, involving a change of the Fe spin direction, deviate since the spin 3/2 is not a complete

representation of the low-energy physics of the Fe atom in the electron model—there is an additional orbital degree of freedom associated with the three electrons residing in the degenerate (xz, yz) orbitals. It could be an artifact of our approximation that neglects the hybridization of the adatom with the surface. Whether present or not, this degree of freedom does not visibly influence the spectra below 10 mV (see Appendix A).

The right panel of Fig. 2 shows the d^2I/dV^2 spectra calculated from Eqs. (3) with $A_{i\Gamma} = A$ and $B_{i\Gamma} = 0$ for $i\Gamma$ corresponding to the Ni atom, and with $A_{i\Gamma} = 0$ and $B_{i\Gamma} = B$ for $i\Gamma$ corresponding to the Fe atom. At large tip–adatom distances (small hopping t), there is just a single peak at 3.5 mV of applied voltage, which progressively splits as the

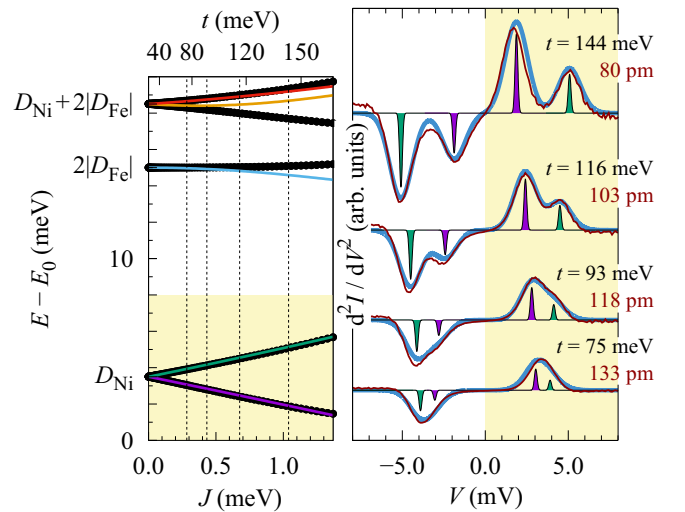


FIG. 2. Nickelocene-terminated tip atop a Fe adatom. Eigenstate energies (left panel) from the electron model (thick black lines) and from the spin model (color lines) are shown as functions of the hopping t and the corresponding exchange J . The d^2I/dV^2 spectra (right panel) are calculated for values of t indicated by vertical lines in the left panel. The colors of the peaks match the colors in the left panel. The thick blue lines are spectra calculated with a Gaussian broadening (1.6 meV FWHM). The thin red lines are the experimental spectra at tip–adatom distances $z = 80, 103, 118$, and 133 pm [15], which are well reproduced with $t = 144, 116, 93$, and 75 meV.

distance decreases and the interaction between the Fe and Ni atoms increases. The individual spectra in Fig. 2 differ only in the value of t . The asymmetry with respect to the voltage polarity (the first peak larger and the second smaller for positive voltages, and vice versa for negative voltages) is a result of Eqs. (3). This is different from the model applied in Ref. [15], in which the asymmetry was controlled by an additional parameter (the polarization of the surface electrode). In the present case, when the hopping t is fitted to a particular splitting of the nickelocene level, the intensities of the d^2I/dV^2 peaks come out automatically and agree very well with the experimental data. This applies to the relative intensities at a particular t as well as to the evolution of the overall intensity of the spectrum as a function of t . For small hopping amplitudes t , the overall intensity scales as t^2 , analogously to the dependence on the tunneling amplitudes $A_{i\Gamma}$ and $B_{i\Gamma}$.

V. ORBITAL MAGNETISM

In the investigations of adatoms with a significant orbital contribution to their magnetic moments, the exchange interaction with the tunneling electrons was traditionally assumed in the bilinear Heisenberg form, either $\mathbf{S} \cdot \mathbf{s}$ [46] or $\mathbf{J} \cdot \mathbf{s}$ [47–49], where $\mathbf{S}$ and $\mathbf{J}$ are the spin and total angular momenta of the adatom, and $\mathbf{s}$ is the spin of the tunneling electron. Under this assumption, the differential conductance has the same structure as our Eqs. (3) but with the intensities of the inelastic transitions being given by the matrix elements of the operators $\hat{\mathbf{S}}$ or $\hat{\mathbf{J}}$ instead of the operator $\hat{O}_{i\Gamma\mu}^{\alpha\beta}$, that is,

$$\mathcal{G}_{\alpha\beta} \sim \sum_{a \in \{x,y,z\}} |\langle \psi_{N\beta} | \hat{S}_a | \psi_{N\alpha} \rangle|^2 \quad (7)$$

for the $\mathbf{S} \cdot \mathbf{s}$ exchange and analogously for the $\mathbf{J} \cdot \mathbf{s}$ exchange [10–13]. When the symmetry of the adatom is such that the eigenstates $|\psi_{N\alpha}\rangle$ are simultaneously also eigenstates of $\hat{S}_z$ (axial symmetry of a sufficiently high order), Eq. (7) implies the selection rule $|\Delta S_z| \leq 1$ for the transitions allowed in the inelastic tunneling [9,10]. Similarly, one arrives at the selection rule $|\Delta J_z| \leq 1$ for the $\mathbf{J} \cdot \mathbf{s}$ exchange when $|\psi_{N\alpha}\rangle$ happen to be eigenstates of $\hat{J}_z$.

It is known, however, that exchange involving orbital moments is more complicated [50,51]. Application of the Heisenberg exchange to $4f$ electrons in the context of the impurity models was criticized already by Coqblin and Schrieffer [52], and deviations from the Heisenberg exchange were also demonstrated experimentally, for instance, in $\text{Yb}_2\text{Pt}_2\text{Pb}$, where the $J_z = \pm 7/2$ doublet behaves like $J_z = \pm 1/2$, which would be impossible with a bilinear exchange [53]. In the context of magnetic adatoms on surfaces, an excitation with $|\Delta L_z| = 4$, where L_z is the out-of-plane component of the orbital momentum, was found in the inelastic electron tunneling spectra of an iron adatom placed above nitrogen (C_{4v} site) on the Cu_2N surface [54].

To visualize the nature of the exchange between the tunneling electron and the nanosystem predicted by our theory, we consider $\hat{\mathcal{H}}_{\text{ns}}$ consisting of a single f shell with a strong spin-orbit coupling corresponding to heavy lanthanides [55] or light actinides [36]. The ground state multiplet of the shell is

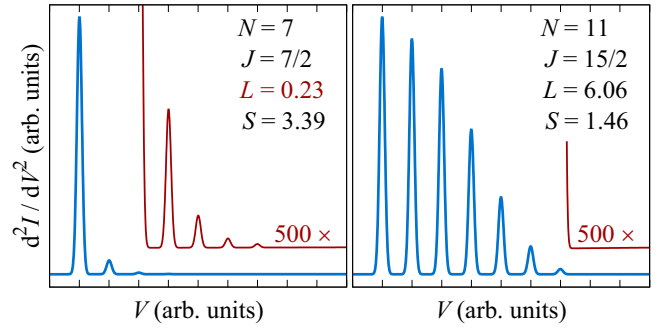


FIG. 3. d^2I/dV^2 spectrum of an f shell split by a magnetic field. The filling of the shell is 7 (left panel) and 11 (right panel). The magnetism of the shell with seven electrons is dominated by spin, hence it displays only a weak deviation from the standard selection rule $|\Delta J_z| \leq 1$.

split by a magnetic field into $2J + 1$ levels $|\psi_{N\alpha}\rangle = |J_z\rangle$, with $J_z = J$ being the ground state. Figure 3 shows its d^2I/dV^2 spectra computed for $A_{i\Gamma} = A$ and $B_{i\Gamma} = B$, which means the electrodes are spherically symmetric around the shell (an artificial setup in the context of STM but advantageous for the effect we intend to illustrate). As long as $2J + 1 \geq 8$, there are seven transitions visible in the spectra, implying the selection rule $|\Delta J_z| \leq 7$. This is consistent with the arguments of Ref. [52] and follows from the maximal possible change of the total angular momentum of the tunneling electron, from $j_z = -7/2$ to $j_z = 7/2$. (The electrode orbitals that couple to the f shell have orbital momentum $\ell = 3$ [18–20], which together with the spin $1/2$ adds up to $j = 5/2$ and $j = 7/2$.) For a general orbital momentum ℓ , the selection rule would be $|\Delta J_z| \leq 2\ell + 1$ (see Appendix B for an additional illustration). The bilinear form of the exchange, $\mathbf{J} \cdot \mathbf{s}$, would allow only one transition (from the ground state $J_z = J$ to the first excited states $J_z = J - 1$). The $\mathbf{S} \cdot \mathbf{s}$ exchange would also allow only this single transition, since the operator $\hat{\mathbf{S}}$ in the matrix elements in Eq. (7) can be replaced by $(g_J - 1)\hat{\mathbf{J}}$, where g_J is the Landé factor, as follows from the Wigner-Eckart theorem (as long as the magnetic field is sufficiently small and does not induce mixing of the ground-state multiplet with the excited-state multiplets).

In the above f -shell example, the Hamiltonian term breaking the spherical symmetry (the magnetic field) is (much) smaller than the spin-orbit coupling. To also illustrate the opposite limit, we pick a d^8 shell in a C_{6v} crystal field. In the d shell (but not in the f or higher shells), this crystal field commutes with the z component of the one-electron orbital momentum, $\hat{\ell}_z$, since only two crystal-field parameters, B_{20} and B_{40} , come into play. By varying the ordering of the one-electron crystal-field levels a_1 ($\ell_z = 0$), e_1 ($\ell_z = \pm 1$) and e_2 ($\ell_z = \pm 2$), one can tune the z component of the many-electron orbital momentum L_z in the d^8 ground state. We select the crystal-field parameters such that the ground-state configuration is $e_1^4 a_1^1 e_2^3 \equiv (xz, yz)^4 (z^2)^1 (x^2 - y^2, xy)^3$, which corresponds to $L_z = \pm 2$ and $S = 1$ (spin triplet), leading to the ground-state degeneracy 6. After introducing a spin-orbit coupling, this ground state splits to three doublets $J_z = \pm 1, \pm 2, \pm 3$. The Hamiltonian no longer commutes with $\hat{L}_z$, $\hat{S}$, and $\hat{S}_z$, only with $\hat{J}_z$, but for a weak spin-orbit coupling the

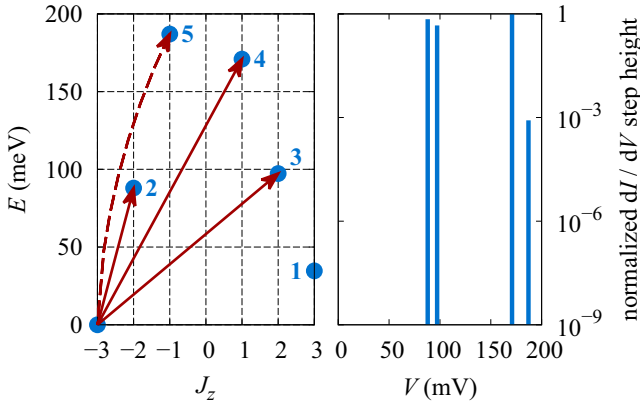


FIG. 4. d^8 shell in a C_{6v} crystal field. The left panel shows the lowest multiplet split by the spin-orbit coupling and by magnetic field. The states with $J_z < 0$ have $L_z \approx -2$, the states with $J_z > 0$ have $L_z \approx 2$. The allowed IETS transitions are indicated by arrows. The right panel shows the normalized height of the corresponding steps in the dI/dV spectrum on a logarithmic scale. The forbidden transition to the first excited state ($\Delta J_z = 6$) has the normalized step height $\sim 10^{-28}$ in our numerical implementation.

Hamiltonian eigenstates $|\psi_{N\alpha}\rangle$ stay close to the eigenstates of $\hat{L}_z$ and $\hat{S}_z$. To completely lift the degeneracy and thus facilitate a straightforward identification of the individual states in the tunneling spectra, we add a magnetic field B_z and also an exchangelike field B_z^{xc} that couples only to spin via the Hamiltonian term $-2\mu_B S_z B_z^{\text{xc}}$ (B_z alone leaves the $J_z = \pm 1$ states nearly degenerate since they have nearly zero magnetic moment μ_z).

The resulting eigenenergies, corresponding to the Hamiltonian parameters based on the Ni^{2+} ion and listed in Table I, are shown in Fig. 4 together with the heights of the steps appearing in the dI/dV spectrum. This spectrum is again computed for $A_{\text{IT}} = A$ and $B_{\text{IT}} = B$. There are four allowed inelastic transitions fulfilling $|\Delta J_z| \leq 2\ell + 1 = 5$. The transition to the second excited state ($\Delta L_z \approx 0$, $\Delta S_z \approx 1$) is the only one of them that would have an appreciable intensity also if we assumed the $\mathbf{S} \cdot \mathbf{s}$ exchange between the d shell and the tunneling electron. The transitions to the third and fourth excited states ($\Delta L_z \approx 4$, $\Delta S_z \approx 1$ or 0) are similar to the transition reported in Ref. [54]. The transition to the fifth excited state ($\Delta L_z \approx 0$, $\Delta S_z \approx 2$, dashed arrow in Fig. 4) is allowed but it is considerably weaker than the other three; it turns out to be proportional to ζ^2 . Finally, the transition to the first excited state would require $\Delta J_z = 6 > 2\ell + 1$ and our calculations indeed indicate that it has a vanishing dI/dV step height.

If the symmetry is reduced from C_{6v} to C_{3v} by adding a crystal-field term corresponding to the parameter B_{43} , the Hamiltonian ceases to commute with $\hat{J}_z$ and its eigenstates $|\psi_{N\alpha}\rangle$ become linear combinations of the eigenstates of $\hat{J}_z$ (and $\hat{S}_z$ and $\hat{L}_z$). Consequently, the difference between the $\mathbf{S} \cdot \mathbf{s}$ exchange and the exchange incorporated in our theory becomes less conspicuous, as transitions to all five excited states shown in Fig. 4 have nonvanishing intensities and it is only their magnitudes that differ between the two cases. Only when the orbital momentum is almost (or entirely) quenched,

like in an iron adatom placed atop copper (C_{2v} site) on the Cu_2N surface [9], the $\mathbf{S} \cdot \mathbf{s}$ exchange represents an accurate approximation.

If the C_{6v} symmetry is maintained but the crystal field is reparametrized such that the ground state configuration is $a_1^2 e_1^3 e_2^3 \equiv (z^2)^2 (xz, yz)^3 (x^2 - y^2, xy)^3$ [56], which corresponds to $L_z = \pm 3$ and $S = 1$, the level diagram remains analogous to Fig. 4, only the quantum numbers shift to $J_z = \pm 2, \pm 3, \pm 4$. As a result, the transitions to the third and fourth excited states disappear as they do not fit within $|\Delta J_z| \leq 2\ell + 1 = 5$ anymore.

VI. SUMMARY

We developed a cotunneling model relevant for the inelastic electron tunneling through nanosystems containing multiple magnetic centers and/or for tunneling spectra measured with STM tips functionalized with a magnetic center. We did not make any assumptions about the magnetic exchange, in particular, it was not reduced to the often-used bilinear form, and hence the model is applicable to magnetic centers with large orbital momenta (like lanthanide or actinide atoms). The general form of the exchange and the consequent less restrictive selection rules also have implications for the decay rates of magnetic states of adatoms, since these rates are often limited by scattering with the surface electrons.

ACKNOWLEDGMENTS

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DATA AVAILABILITY

The data that support the findings of this article are openly available [57].

APPENDIX A: ON THE ANISOTROPY OF FE ADATOM ON THE CU(100) SURFACE

In the discussion of the IETS spectra of the Fe adatom on the Cu(100) surface measured with a nickelocene-terminated STM tip, we assumed that the Fe anisotropy is large so the Fe spin is essentially frozen in the $S_{z,\text{Fe}} = \pm 3/2$ state. This facilitated the reduction of the two-spin model, Eq. (6), to a model for the Ni spin only. Verlhac *et al.* [15] alluded to this single-spin model being applicable also for small Fe anisotropy as long as $|D_{\text{Fe}}| > k_B T$. Here we test this conjecture by explicitly comparing the predictions of our IETS theory in two scenarios: $|D_{\text{Fe}}| > D_{\text{Ni}}$ and $|D_{\text{Fe}}| < D_{\text{Ni}}$.

We keep the parameters of the Ni $3d$ shell the same as before but we alter the crystal field of the Fe $3d$ shell; we tune it to give $(xy)^2(x^2 - y^2)^2(xz, yz)^2(z^2)^1$ as the ground-state configuration, which supports the out-of-plane easy axis like the DFT-based configuration employed earlier. The

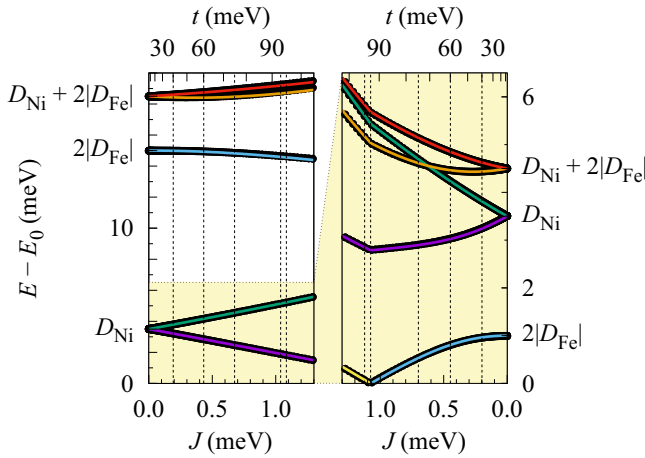


FIG. 5. Eigenstate energies calculated in the electron model (thick black lines) and in the corresponding spin model (color lines) as functions of the hopping t and the corresponding exchange J . Two scenarios of the anisotropy parameters are compared: $|D_{\text{Fe}}| > D_{\text{Ni}}$ (left panel) and $|D_{\text{Fe}}| < D_{\text{Ni}}$ (right panel). The vertical lines indicate the t values, for which the d^2I/dV^2 spectra are shown in Figs. 6 and 7. Note the different ranges of the vertical axes and the different directions of the horizontal axes in the two panels.

numerical values of the Wybourne parameters B_{kq} , corresponding to anisotropy parameters $D_{\text{Fe}} = -7.5$ meV and $D_{\text{Fe}} = -0.5$ meV, are listed in Table I. Figure 5 compares the eigenstate energies computed in the electron model $\hat{H}_{\text{ns}}$ and in the corresponding spin model $\hat{H}_{\text{spin}}$, Eq. (6). Unlike Fig. 2, they now match almost perfectly since the present configuration of the Fe 3d shell avoids the extra orbital degree of freedom associated with the 3/4 filling of the doubly degenerate (xz , yz) orbitals. Compared to Fig. 2, the prefactor in the relation $J \sim t^2/U$ is now different (and it is also slightly different in each of the two panels in Fig. 5).

Figure 6 shows the d^2I/dV^2 spectra calculated from Eqs. (3) in the same way as the spectra plotted in Fig. 2. The present spectra obtained for $|D_{\text{Fe}}| > D_{\text{Ni}}$ are almost indistinguishable from the spectra in Fig. 2 despite being calculated with a substantially different crystal-field potential. It is not so surprising, however, since the Fe degrees of freedom are frozen in the same spin state $S_{z,\text{Fe}} = \pm 3/2$ in the whole voltage range plotted in the figures, and these spectra are thus only a very limited probe of the Fe crystal field.

The d^2I/dV^2 spectra corresponding to $|D_{\text{Fe}}| < D_{\text{Ni}}$ are very different since the excitations involving the Ni and Fe spins are mixed together in this case. Their shape is clearly incompatible with the experimental data [15]. These spectra are, however, similar to the spectra measured with a nickelocene-terminated tip on Cr atoms embedded in metal-organic polymers, which have a spin $S_{\text{Cr}} = 2$, out-of-plane easy axis, and a small anisotropy parameter $D_{\text{Cr}} \approx -0.23$ meV [16].

To bring the spectra of the scenario with $|D_{\text{Fe}}| < D_{\text{Ni}}$ closer to the experiment, there would have to be a mechanism suppressing the excitations involving the Fe spin. Essentially, the tunneling electrons would have to travel along a path that avoids the Fe 3d shell, passing instead through some orbital(s) also centered at the Fe atom but being more diffuse than the 3d

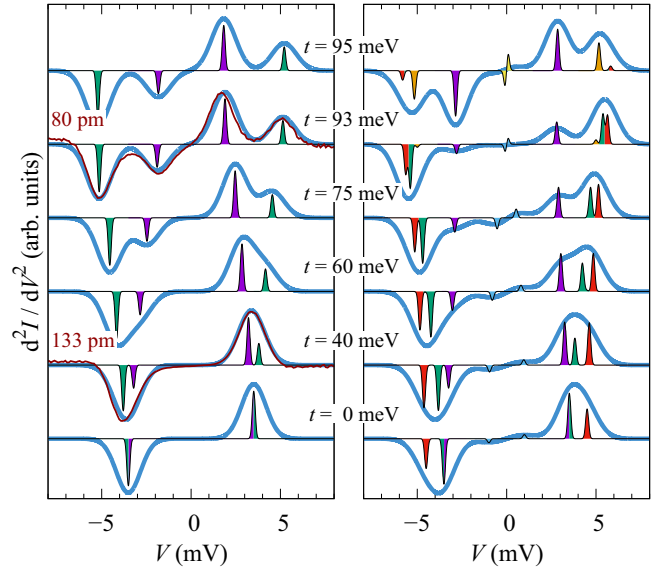


FIG. 6. Sets of d^2I/dV^2 spectra calculated for a nickelocene-terminated STM tip atop the Fe adatom assuming $|D_{\text{Fe}}| > D_{\text{Ni}}$ (left panel) and $|D_{\text{Fe}}| < D_{\text{Ni}}$ (right panel). The colors of the peaks match the colors in Fig. 5. The orange peak in the right panel has a vanishingly small intensity for $t \leq 75$ meV but it is not forbidden. The thick blue lines are spectra calculated with a Gaussian broadening (1.6 meV FWHM). The thin red lines in the left panel are the experimental data obtained at tip-adatom distances $z = 80$ pm and $z = 133$ pm [15]. The two topmost spectra in the right panel are taken just before and just after the ground state and the first excited state interchange. The spectra are normalized to the largest peak independently at each t to magnify the details at small t .

shell, for instance, the 4s orbitals. Being more diffuse implies that these orbitals should be substantially hybridized with the electronic states of the surface. The simplest description we can build amounts to considering these extra orbitals as a part of the surface electrode, completely decoupling the Fe 3d shell from the surface, and introducing tunneling from the surface directly to the Ni 3d shell. This means setting $A_{i\Gamma} = A$ and $B_{i\Gamma} = B$ for $i\Gamma$ corresponding to the Ni atom, and $A_{i\Gamma} = 0$ and $B_{i\Gamma} = 0$ for $i\Gamma$ corresponding to the Fe atom.

The d^2I/dV^2 spectra calculated in such an alternative tunneling setup are shown in Fig. 7. The Fe-related excitations are indeed suppressed and the spectra reflect mostly just the Nc level split by the exchange field in both scenarios, $|D_{\text{Fe}}| > D_{\text{Ni}}$ and $|D_{\text{Fe}}| < D_{\text{Ni}}$. The peak intensities, however, are not consistent with the experiment—the spectra are antisymmetric with respect to the polarity of the tip-surface voltage V . Since the current does not pass through the Fe 3d shell now, no equivalent of the apparent polarization of the surface electrode is generated and hence the mechanism causing the spectra asymmetry is lost. Another aspect making the $|D_{\text{Fe}}| < D_{\text{Ni}}$ case inconsistent with the experiment is the asymmetric splitting of the Nc level around its energy at large tip-adatom distances ($t = 0$ meV), already apparent in Fig. 5.

Putting all these observations together, we can conclude that the IETS spectra reported by Verlhac *et al.* [15] represent an evidence for the anisotropy D_{Fe} of the Fe adatom at the hollow site of the Cu(100) surface to be negative and larger

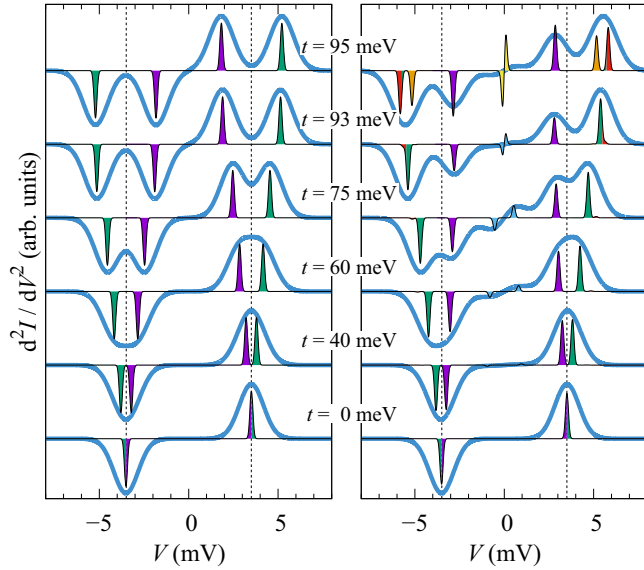


FIG. 7. Sets of d^2I/dV^2 spectra calculated for a nickelocene-terminated tip atop the Fe adatom assuming $|D_{\text{Fe}}| > D_{\text{Ni}}$ (left panel) and $|D_{\text{Fe}}| < D_{\text{Ni}}$ (right panel), when the tunneling current does not pass through the Fe 3d shell. Everything else is the same as in Fig. 6.

than 5 meV. Precise determination of the actual magnitude of D_{Fe} would require an experimental detection of the excitations corresponding to changes of the Fe spin direction.

APPENDIX B: SELECTION RULE FOR THE ORBITAL MOMENTUM

To analytically illustrate the selection rule for the total angular momentum, deduced numerically in Sec. V, we consider one spinless electron in a d shell (orbital momentum quantum number $\ell = 2$). In the absence of spin, the shell has only the orbital momentum. The tunneling proceeds via an empty shell (the $1/\epsilon$ term in the following formula) and via

TABLE II. The eigenstates and eigenenergies of a d shell hosting spinless electrons. Here N is the filling of the shell, $|LM\rangle$ are states with the total orbital momentum L and its projection M on the quantization axis. The other quantities are defined in the text. For the singly occupied shell to be the ground state, ϵ must be negative and U larger than $|\epsilon|$.

$N = 0$		$N = 1$		$N = 2$	
$ 0\rangle$	0	$ 2, M\rangle$	ϵ	$ 3, M\rangle$	$2\epsilon + U$
				$ 1, M\rangle$	$2\epsilon + U + U'$

states with two electrons (all the other terms). The transition operator defined in Eq. (3c) can be transformed to

$$\begin{aligned} \hat{O}_{mm'}^{\alpha\beta} = & \left(\frac{1}{\epsilon} - \frac{1}{\epsilon + U} \right) \hat{d}_m^\dagger \hat{d}_{m'} + \frac{1}{\epsilon + U} \delta_{mm'} \\ & + 2 \left(\frac{1}{\epsilon + U + U'} - \frac{1}{\epsilon + U} \right) \\ & \times \sum_{Mnn'} \langle 2n', 2m' | 1M \rangle \langle 1M | 2n, 2m \rangle \hat{d}_n^\dagger \hat{d}_n, \end{aligned} \quad (\text{B1})$$

where $\epsilon < 0$ is the single-particle energy of the atomic level (the energy of the shell filled with one electron), $U > |\epsilon|$ and U' come from the Coulomb repulsion, and $\langle \ell_1 m_1, \ell_2 m_2 | LM \rangle$ are Clebsch-Gordan coefficients. In terms of the Slater parameters, U and U' read as $U = F_0 - 8F_2/49 - F_4/49$ and $U' = 15F_2/19 - 25F_4/147$. The states of the d shell relevant for the transition operator are listed in Table II. The voltage bias V was assumed to be much smaller than U or $|\epsilon|$ and was neglected. The form of Eq. (B1) shows that transitions from any m' to any m are possible. This observation is not limited to d shells since the empty-shell term $\epsilon^{-1} \hat{d}_m^\dagger \hat{d}_{m'}$ is the same irrespective of ℓ , and hence we have $|\Delta m| \leq 2\ell$ for any spherically symmetric shell occupied with a single electron. The same formula as Eq. (B1) (for $U' = 0$) was discussed in the context of Ce impurities in Ref. [52].

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