Ho on Pt(111) as a single-atom memory bit:
A quantum master equation analysis

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Due to underlying symmetries the two degenerate angular-momentum ground states of a single holmium atom (with \( J = 8 \)) on a Pt(111) surface have exceptionally long lifetimes, as observed in recent scanning tunneling microscopy studies. This opens perspectives for the application as a single-atom memory bit. For control and read-out the atom is coupled to electronic contacts. Hence the spin dynamics of the system is governed by a quantum master equation. In general it cannot be reduced to a classical master equation in the basis of the unperturbed crystal-field Hamiltonian. Rather, depending on parameters and control fields, “environment induced superselection” principles choose the appropriate set of basis states, which in turn determines the specific relaxation channels and lifetimes. Our results suggest that in ideal situations the lifetimes should be even longer than observed in the experiment. We, therefore, investigate the influence of various perturbations. We also study the initialization process of the state of the Ho atom by applied voltage pulses and conclude that fast, high fidelity writing into the memory, on a 100ns timescale, should be possible.

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I. INTRODUCTION

An ultimate boundary of miniaturization of information technology is reached when single atoms are used as memory media. In this respect the experiment of Miyamachi et al. [1] represented an important milestone, demonstrating lifetimes of several minutes for the two degenerate ground states of a single holmium atom positioned on a Pt(111) surface. This is many orders of magnitude longer than lifetimes measured for single Co/Fe atoms on Pt(111) [2, 3] or other magnetic adatoms on a metallic surface [4]. The two Ho ground states differ by the \( J_z \)-projection of the magnetic moment of the atom with \( J = 8 \) pointing into or out of the surface. A related giant magnetic anisotropy of single adatoms had been observed earlier for Co atoms on Pt(111) [5]. For the crystal-field Hamiltonian with parameters as determined in Ref. [1], the two ground states of the Ho atom have \( J_z \approx \pm 8 \). Their long lifetimes result from a combination of symmetries and specific properties of the system [1]. We should mention that in recent work for Ho on Pt(111), Donati et al. [6] arrived at different crystal-field parameters, leading to ground states with \( J_z \approx \pm 6 \), for which we find much shorter lifetimes.

In this paper we analyze the system Ho on Pt(111) in greater detail. Most of our work is based on the crystal-field Hamiltonian with parameters as determined in Ref. [1], but we also compare with the situation obtained for the parameters of Ref. [6]. For read-out and control the Ho atom is coupled to electronic reservoirs formed by the metal substrate and the spin polarized STM tip. The description of this dissipative system is based on a quantum master equation for the reduced density matrix for the angular momentum states, which accounts for the influence of the electronic contacts and the applied voltage. For low voltages the description reduces to a rate equation in the eigenbasis of the unperturbed Hamiltonian, which are specific superpositions of angu-
lar momentum states. However, for larger voltages the coherence of these superposition states is destroyed, and the relevant states are the steady state solutions of the full dissipative quantum master equation. This is an example for what has been called “environment-induced superselection” (or short “einselection”) principle [8, 9]. In the considered system the choice of the appropriate basis depends strongly on the voltage. Switching the voltages also allows initializing the systems in a specific ground state, which is useful for experiments and when using the system as memory.

The quantitative comparison with the experiments requires assumptions about a number of parameters, which we explore in this paper in detail. For the comparison we also present new experimental data on the dependence of lifetimes of the system on the tip voltage.

II. THE MODEL

A. The crystal-field Hamiltonian and eigenstates

The properties of a Ho adatom on a Pt(111) surface had been investigated in Refs. [1, 10, 11]. The Ho atom has strong spin-orbit coupling, therefore the total angular momentum is a good quantum number with value \( J = 8 \), leading to 17 states in the multiplet to be studied. A single adatom on a crystal structure with trigonal symmetry can be described by a crystal field Hamiltonian adjusted to the symmetries [10],

\[
H_{CF} = \sum_{n=2,4,6} \sum_{m=-n}^{n} B_{n}^{m} O_{n}^{m} \tag{1}
\]

\[
\approx B_{2}^{0} \cdot 3 J_{z}^{2} + B_{1}^{3} \cdot \frac{1}{4} \left[ J_{z} (J_{z}^{2} + J_{z}^{3}) \right]_{+} + \ldots
\]

The \( B_{n}^{m} \) are crystal field parameters, which in Ref. [11] were determined from \textit{ab-initio} calculations and compared with experiment, and \( O_{n}^{m} \) are the Stevens operators containing powers of \( J_{z} \), \( J_{z}^{2} \) and \( J_{z}^{3} \). angular momentum operators of the Ho atom [11]. Due to the symmetry the operators \( J_{z} \) and \( J_{z}^{2} \) appear in powers of multiples of three. Above, only the first two terms are shown explicitly (with \([ , ]_{+}\) denoting the anti-commutator); further ones are listed in the Appendix.

The eigenstates of the crystal field Hamiltonian \( H_{CF} \) can be divided into three families of states, \( |\Psi_{+}^{m}\rangle \), \( |\Psi_{-}^{m}\rangle \), and \( |\Psi_{0}^{m}\rangle \). Each one of these states is a superposition of different \( J_{z} \) eigenstates with magnetic quantum numbers differing by multiples of 3. The lower index \( m \) of each state, with \(-8 \leq m \leq 8\), denotes the dominantly contributing \( J_{z} \) eigenstate. In Fig. [2] we plot the eigenenergies versus the \( J_{z} \) expectation value. They are marked by circles, squares and triangles for the three families \(+, -, 0\). Since the dominant contribution to the eigenenergies arises from the first term \( -J_{z}^{2} \) the energies fit approximately on an inverted parabola. Note that by plotting the energy versus the expectation value of \( J_{z} \) we can also represent arbitrary superposition states of the aforementioned basis states, which is useful for the following discussion.

The two degenerate ground states of the system \( |\Psi_{+}^{0}\rangle \) and \( |\Psi_{-}^{0}\rangle \), with differing \( J_{z} \) projection of the angular moment into or out of the surface, belong to different families (+ and −). The same applies for the first excited states \( \left| \Psi_{+}^{7} \right\rangle \) and \( \left| \Psi_{-}^{7} \right\rangle \), as well as for various higher ones. These superposition states are formed by degenerate \( J_{z} \)-eigenstates. In contrast, the states \( |\Psi_{+}^{0}\rangle \) and \( |\Psi_{0}^{0}\rangle \), belonging to the 0–family, are superpositions made up of degenerate \( J_{z} \)-eigenstates, coupled by the operators \( O_{4}^{\pm}, O_{6}^{\pm} \) and \( O_{6}^{0} \). They naturally split into symmetric and antisymmetric (s,a) combinations, both with vanishing \( \langle J_{z} \rangle \). The same applies for \( |\Psi_{3a}^{0}\rangle \) and \( |\Psi_{3a}^{6}\rangle \).

B. Spin-dependent electron scattering

For control and read-out, the Ho adatom is coupled to a spin polarized STM tip. The electronic reservoirs influence the dynamics of the system by the scattering of electrons in the electrodes from the atom and by the tunneling of electrons between tip and bulk substrate via the atom (see Fig. [4]). Accordingly the total Hamiltonian consists of three parts, \( H = H_{S} + H_{B} + H_{C} \), describing the system, the electron baths in the substrate and tip of the STM, and the coupling terms,

\[
H_{S} = \hat{H}_{CF} + g_{J} \mu_{B} \mathbf{B} \cdot \mathbf{J}, \tag{2}
\]

\[
H_{B} = \sum_{\sigma=\uparrow, \downarrow, k} \varepsilon_{\sigma k} c_{\sigma k}^{\dagger} c_{\sigma k}, \tag{3}
\]

\[
H_{C} = \sum_{k, \alpha, \alpha'} \sum_{\sigma=\uparrow, \downarrow} \sum_{\alpha=\uparrow, \downarrow} \sum_{k' k''} \sum_{\alpha=\uparrow, \downarrow} \sum_{\alpha=\uparrow, \downarrow} \sum_{k' k''} \sum_{\alpha=\uparrow, \downarrow} \sum_{\alpha=\uparrow, \downarrow} \left[ J_{+} c_{k_{\alpha} k'_{\alpha} \uparrow}^{\dagger} c_{k_{\alpha} k'_{\alpha} \downarrow} + J_{-} c_{k_{\alpha} k'_{\alpha} \downarrow}^{\dagger} c_{k_{\alpha} k'_{\alpha} \uparrow} \right] + 2J_{z} \left( c_{k_{\alpha} k'_{\alpha} \uparrow}^{\dagger} c_{k_{\alpha} k'_{\alpha} \uparrow} - c_{k_{\alpha} k'_{\alpha} \downarrow}^{\dagger} c_{k_{\alpha} k'_{\alpha} \downarrow} \right). \tag{4}
\]
In [2] we added the contribution due to an applied or stray magnetic field $\vec{B}$, with $q_1$ being the Landé-factor and $\mu_B$ the Bohr magneton. The bath electron creation (annihilation) operators are $c_{\alpha \sigma}^\dagger$ ($c_{\alpha \sigma}$), where $\alpha$ can be $T$ or $B$ for tip or bulk. Here we concentrate on the interaction of the spins of the electrons with the angular momentum $\vec{J}$ of the atom, which leads to scattering and tunneling processes with or without spin flip with amplitudes $t_{kk'}^{\sigma\sigma'}$ described by the three terms in $H_C$. For $\alpha = \alpha' = B$ these terms describe the scattering of a bath electron, while for $\alpha \neq \alpha'$ they describe tunneling from the tip via the Ho atom to the bulk or back. In the following we will ignore the weak scattering of tip electrons, i.e. we set $t_{kk'}^{TT} = 0$.

The eigenstates have the property that two eigenstates with the same energy but from different families have vanishing matrix elements $\langle \Psi_{m\sigma}^\dagger | J_\nu | \Psi_{m'\sigma'} \rangle = 0$ for $\nu \in \{ +, -, z \}$, $\sigma = \pm$ and all $m$. It is a consequence of two properties of the system: First, the $C_3v$ symmetry of the adsorption site, which leads to the Stevens-operators introduced above with operators $J_+ \text{ and } J_-$ appearing in powers of three. Second, the time-reversal symmetry for $\vec{B} = 0$ with the following properties of the time-reversal operator $T$ (see Ref. [1]),

$$T^2 = 1, \quad T J_\nu = -J_\nu T, \quad T | \psi_{m\sigma} \rangle = | \psi_{-m\sigma} \rangle,$$

$$\langle \chi | \phi \rangle = \langle T \phi | T \chi \rangle = \langle T \chi | T \phi \rangle^*.$$

(5)

From these relations we find $\langle \psi_{m\sigma}^\dagger | J_\nu | \psi_{-m\sigma} \rangle = 0$ since

$$\langle \psi_{m\sigma}^\dagger | J_\nu | \psi_{-m\sigma} \rangle = \langle T \psi_{-m\sigma} | T J_\nu | \psi_{m\sigma} \rangle^* = - \langle \sigma_{m\sigma}^\dagger | J_\nu T \sigma_{m\sigma} \rangle^*$$

$$= - \langle \psi_{m\sigma}^\dagger | J_\nu | \psi_{-m\sigma} \rangle^* = - \langle \psi_{-m\sigma}^\dagger | J_\nu | \psi_{m\sigma} \rangle.$$

(6)

Thus, a transition between the two ground states with $m \approx \pm 8$ cannot be induced by a single electron scattering, which is the origin of their observed long lifetimes.

On the other hand, at non-zero temperature $T \neq 0$ and under the influence of an applied voltage $U$, scattering of electrons may lead to transitions to the first excited states and beyond, and eventually to transitions between the two ground states. Additionally, time-reversal symmetry breaking terms in the Hamiltonian such as a magnetic field give rise to direct transitions between the ground states. This leads to a finite relaxation time $T_1$, which has been probed in the experiment and will be studied in the following sections. In a later section we will also investigate the decoherence time $T_2$, i.e., the time scale for the decay of a coherent superposition of the two ground states.

The temperature in the experiments was as low as 0.7 K (i.e., $k_B T \approx 0.060$ meV), whereas the typical system energy, i.e. the first excitation energy is 7.7 meV [3]. Thus, the system is clearly in the quantum regime.

### III. QUANTUM MASTER EQUATION

The description of the system in the quantum regime under the influence of the electronic reservoirs requires solving the reduced quantum master equation appropriate for open quantum systems [12, 13],

$$\dot{\rho}(t) = i [\rho(t), H_S(t)] + \int_0^t \Sigma(t - t') \rho(t'). \quad (7)$$

Here and below we set $\hbar = 1$. The influence of the two electronic baths enters in the dissipative kernel $\Sigma(t - t')$. In Lindblad form with Born-Markov approximation the quantum master equation for the 17 states of the system reduces to

$$\dot{\rho} = i [\rho(t), H_S(t)] - \sum_{\nu,\nu'} \int_0^\infty dt' \left\{ [J_{\nu}(t) J_{\nu'}(t') \rho(t) - J_{\nu'}(t) J_{\nu}(t') \rho(t)] C^{\alpha\alpha'}_{\nu\nu'}(t - t') + [\rho(t) J_{\nu}(t') J_{\nu'}(t) - J_{\nu}(t) \rho(t) J_{\nu'}(t')] C^{\alpha\alpha'}_{\nu'\nu}(t - t') \right\},$$

with dissipative kernel expressed by correlation functions

$$C^{\alpha\alpha'}_{\nu\nu'}(t) = \sum_{k,k'} | t_{kk'}^{\nu\nu'} |^2 \langle s_{kk'\nu}(t) s_{k'k\nu'}(0) \rangle$$

(9)

with

$$s_{kk'\nu}^{\alpha\alpha'} = c_{k\nu}^{\alpha} \bar{c}_{k'\nu'}^{\alpha'}, \quad s_{kk'\nu'}^{\alpha\alpha'} = c_{k\nu}^{\alpha} \bar{c}_{k'\nu'}^{\alpha'},$$

$$s_{kk'z}^{\alpha\alpha'} = 2 \left( c_{k\nu}^{\alpha} \bar{c}_{k'\nu'}^{\alpha'} - c_{k\nu}^{\alpha'} \bar{c}_{k'\nu'}^{\alpha} \right).$$

(10)

Assuming $t_{kk'}^{\nu\nu'} \approx t^{\alpha\alpha'}$ and introducing the spin-dependent electron densities of states at the Fermi-edge $N^\alpha_{\nu}$ with $\sigma \in \{ \uparrow, \downarrow \}$ we obtain the Fourier transformed of the correlation functions. They are evaluated at the energy differences of the atomic system, $\Lambda_{nm} = E_m - E_n$, and shifted by the applied voltage,

$$\tilde{C}^{\alpha\alpha'}_{\nu\nu'}(\pm \Lambda_{nm}) = | t^{\alpha\alpha'} |^2 N^\alpha_{\nu} N^\alpha_{\nu'} \zeta(\pm \Lambda_{nm} + e(U^\alpha - U^{\alpha'})),$$

$$\tilde{C}^{\alpha\alpha'}_{-\nu\nu'}(\pm \Lambda_{nm}) = | t^{\alpha\alpha'} |^2 N^\alpha_{\nu} N^\alpha_{\nu'} \zeta(\pm \Lambda_{nm} + e(U^\alpha - U^{\alpha'})),$$

$$\tilde{C}^{\alpha\alpha'}_{z\nu\nu'}(\pm \Lambda_{nm}) = 4 | t^{\alpha\alpha'} |^2 \left( N^\alpha_{\uparrow} N^\alpha_{\downarrow}^* + N^\alpha_{\downarrow} N^\alpha_{\uparrow}^* \right) \zeta(\pm \Lambda_{nm} + e(U^\alpha - U^{\alpha'})).$$

(11)

Here we introduced

$$\zeta(x) = \int f(E) \left[ 1 - f(E - x) \right] dE = \frac{x}{\exp[x/(k_B T)] - 1},$$

and $f(E) = [e^{E/(k_B T)} + 1]^{-1}$ is the Fermi function. We set the bulk potential $U_B$ to zero. As usual in the context of the tunneling magneto-resistance we define the tip polarization $\eta = (P_1 - P_2)/(P_1 + P_2) \in [-1, 1]$, where the spin up/down populations are proportional to the
densities of states \( P_{1/4} \propto N_{1/4}^T = N^T \cdot \frac{1}{2} (1 \pm \eta) \). The bulk electrode is assumed to be non-polarized, hence \( N_{1/4}^B = N^B \). For convenience we introduce the parameters \( c_{TB} = |T^B|^2 N^B N^T \) and \( c_{BB} = |B^B|^2 (N^B)^2 \). In the following discussions we will first ignore the scattering of bulk electrons from the Ho atom \((C_{\rho \rho \rho}^B = 0)\), but we will analyze its influence in section V A.

The quantum master equation \( \dot{\rho}(t) = \mathcal{L}(\rho) \) for the density matrix can be rewritten in the form \( \dot{\rho}(t) = M \rho(t) \) where the density matrix \( \rho \) (here \( 17 \times 17 \)) is arranged as a vector \( \vec{\rho} \) (with 289 components) and all the dynamics, coherent and dissipative, are included in the components of the large \((289 \times 289)\) matrix \( M \) (for details see Appendix). The spectral decomposition of this matrix, \( M \vec{\rho}_n = m_n \vec{\rho}_n \), gives access to various relaxation rates. It also yields the steady-state populations \( \vec{\rho}(t \to \infty) = \vec{\rho}_{ss} = \vec{\rho}_0 \), which is the eigenvector corresponding to the zero eigenvalue \( m_0 = 0 \) \([14]\).

If the system behaves sufficiently classically, it is possible to reduce the quantum master equation to rate equations for the populations \( P_t \) of the different states

\[
\frac{d P_i}{dt} = \sum_j (\Gamma_{ji} P_j - \Gamma_{ij} P_i),
\]

with \( \Gamma_{ji} \) describing the transition rates between the different states. Such a reduction is possible if the coherences, i.e., the off-diagonal components of the density matrix decay much faster than non-equilibrium populations. This question remains, what is the appropriate basis to decouple the coherences and populations. One option for this basis are the eigenstates of \( H_{CF} \). It is the appropriate choice if the influence of the bath is weak, and the eigenstates are only little affected by its presence. The reduction to rate equations, which had been used, e.g., in Refs. [13, 14] allows an easy interpretation of transition channels.

However, in the present problem this reduction is not allowed in general for the 0-family eigenstates of the Hamiltonian. Due to degeneracies they are superpositions of several \( J_z \) basis states with similarly large amplitudes. In much of the relevant parameter space their weak coherent coupling is destroyed by the baths. This scenario has been termed “environment-induced superselection” principle by Zurek [7, 8]. Decoherence selects favored “pointer” states which are stable under the influence of the environment [14]. These states are the steady-state eigenstates of the full quantum master equation. The properties of the two sets of basis states are compared in Fig. 2.

### IV. RELAXATION TIME \( T_1 \)

If the system is mainly in one of the two degenerate ground states, the relaxation time \( T_1 \) towards the steady state is given by the smallest non-zero eigenvalue of the matrix \( M \), corresponding to the eigenvector \( \vec{\rho}_1 = (1, 0, ..., 0, -1)^T \). (Here we assumed an ordering such that the first and last entries of the eigenvector are the ground states). The inverse of the \( T_1 \) time, \( 1/T_1 = -m_1 = \Gamma_{-8\to+8} + \Gamma_{+8\to-8} \), accounts for all relaxation channels from one ground state to the other. Note that the switching rate \( \Gamma_{-8\to+8} \) from \( |\Psi_{-8}\rangle \) to \( |\Psi_{+8}\rangle \) accounts for the direct transition but also all those

![FIG. 3. a) Relaxation time \( T_2 \) and decoherence time \( T_2 \) of the two ground states versus the applied voltage \( U \) obtained from the full quantum master equation (full lines) and the rate equation \( \dot{\rho}(t) = \mathcal{L}(\rho) \) based on \( H_{CF} \) eigenstates (dotted lines). A weak magnetic field \( B_z = 10^{-8} \) T is applied, the temperatures are \( T = 0.7 K, T = 1.4 K, T = 3.5 K \) and \( T = 7 K \), and the coupling strength is \( c_{TB} = 8.53 \cdot 10^8 (\text{meV s})^{-1} \). b) Energy expectation values versus the expectation values of \( J_z \) for the steady states of the full quantum master equation and for the \( H_{CF} \) eigenstates at \( T = 0.7 K \) for \( U = 3 \) mV and \( U = 7 \) mV. c) Relaxation time \( T_1 \) of the two ground states versus the coupling strength \( c_{TB} \) as obtained from the full quantum master equation and from the rate equation \( \dot{\rho}(t) = \mathcal{L}(\rho) \) based on the eigenstates of \( H_{CF} \) for \( B_z = 10^{-8} \) T and \( T = 0.7 K \).]
via excited states. It differs from the rate $\Gamma_{-ss}$ of the rate equations\[^{12}\], which describes only the direct transition. The relation between the two switching rates $\Gamma_{-s+s}$ and $\Gamma_{s-s}$ (and related lifetimes) follows from the steady state populations $P_{-s}$ and $P_{s}$ of the two ground states, $\tau_{-s}/\tau_{s} = \Gamma_{-s+s}/\Gamma_{s-s} = P_{-s}/P_{s}$.

### A. Voltage dependence

To compare with the experiments of Ref.\[^1\] we need to know the coupling strength for tunneling of the reservoir electrons via the Ho atom. For this purpose we calculate the current $I_{th}$ from the dissipative part of the master equation (for details see Appendix). By comparison with the experiment we should be able to determine the coupling strength $c_{TB}$. However, the current $I_{th}$ describes only the current where electrons scatter due to the spin – angular momentum interaction. The total current includes a ‘leakage’ current $I_{exp} = I_{th} + I_{leak}$ due to electrons tunneling directly between tip and bulk or due to electrons scattering with shells other than the 4f shell which forms the basis of the considered angular momentum states. By comparing the current which involves spin flips and accordingly depends on the spin state of the Ho atom with the state-independent current we get a rough estimate. For the following discussion we assume that $I_{th}$ amounts for roughly 10% of the total current $I_{exp}$, i.e. $I_{th} = 0.1$ nA. For $U = 3$ mV this is achieved by a coupling strength of $c_{TB} = 8.53 \cdot 10^3$ (meV s)$^{-1}$.

We are now ready to analyze the dependence of the relaxation time on the applied voltage. In Fig. 3 a) we plot the results for the temperature $T = 0.7$ K chosen in the experiments, and for comparison at several higher temperatures $T = 1.4$ K, $T = 3.5$ K and $T = 7$ K. We compare the $T_1$ time, as obtained from the numerical solution of the full quantum master equation, and the result obtained from the approximate rate equations\[^{12}\] in the basis of $H_{CF}$ eigenstates. Similarly we compare in Figs. 3 b) the $J_z$ expectation values of the steady state solutions of the master equation and those of the $H_{CF}$ eigenstates for two different values of $U$. For reasons of numerical stability we include in all our simulations the effect of a very weak magnetic field applied in z-direction ($B_z = 10^{-8}$ T). Otherwise the two ground states get completely decoupled within the numerical precision, and numerical divergences appear, or the reduced density matrix is no longer positive semidefinite.

Focusing on the low temperature, $T = 0.7$ K, we note that for low voltages, $U \lesssim 3$ mV, the six lowest lying steady states of the full quantum master equation have very similar properties as the $H_{CF}$ eigenstates. In this regime transitions between the two ground states $|\Psi_{s}^+\rangle$ to $|\Psi_{-s}^+\rangle$ are caused mostly by the (weak) symmetry-breaking magnetic field and are thus voltage independent. The full master equation yields shorter lifetimes (higher rates) than the rate equation in this regime, because of additional coherent transitions contained in the former.

At higher voltages we observe for $T = 0.7$ K and $T = 1.4$ K in (the semi-log plot of) Fig. 3 a) an exponentially activated behavior. In this regime the full master equation and the rate equation yield very similar results. Here the main switching channel is via the first excited states, $|\Psi_{7}^+\rangle$ or $|\Psi_{7}^-\rangle$, followed by a fast decay to the other ground state on the other side of the parabola. Since the first step is the bottleneck of the process we have $1/T_1 \approx \Gamma_{s7} + \Gamma_{-s7}$. For an estimate we ignore the effect of the tip polarization and of a magnetic field (i.e. $\Gamma_{s7} \approx \Gamma_{-s7}$) and get

$$\Gamma_{s7} = c_{TB} |\langle \Psi_{7}^- | J_{-} | \Psi_{s}^+ \rangle |^2 \cdot \zeta (E_{7} - E_{s} + eU) \approx 16 c_{TB} \frac{(E_{7} - E_{s} + eU)}{e (E_{7} - E_{s} + eU) / k_{B} T - 1} \propto e^{-eU/k_{B}T}.$$  

For still higher voltages, $U > 7$ mV, the results obtained in the two approaches differ again. In this regime excitations to the symmetric and anti-symmetric $H_{CF}$-eigenstates $|\Psi_{0a}^\pm\rangle$ and $|\Psi_{0b}^\pm\rangle$ become possible. These two states have high transition rates between each other and thus could provide a ‘shortcut’ for the decay. However, in the full master equation these superpositions states are split into $|\Psi_{0a}^\pm\rangle$ and $|\Psi_{0b}^\pm\rangle$ due to the dephasing by the scattering electrons (see Fig. 3 b)). Thus the shortcut is no longer open, which reduces the transition rates.

For even higher voltages, $U > 8.6$ mV, tunneling electrons have enough energy to overcome also the second energy excitation gap of $\Delta E_{07} = E_{0} - E_{7} \approx 8.6$ meV, which is the largest gap of the system. From this point on, sequential scattering over the top of the parabola is the main transition channel, and the slope of the $T_1(U)$ function changes.

At higher temperatures, the different regimes get smeared out, as can be seen in the plot of Fig. 3 especially for $T = 3.5$ K and $T = 7$ K. In this regime the main transition channel is always via higher excited states. For voltages larger than $U \approx 9$ mV the results for all temperatures are very similar, because in all cases most of the electron scattering leads to the transition over the top of the parabola. Again, the rate equations overestimate the role of transitions via the ‘shortcut’ states $|\Psi_{0+}^\pm\rangle$, $|\Psi_{0-}^\pm\rangle$, $|\Psi_{+3}^\pm\rangle$ and $|\Psi_{-3}^\pm\rangle$.

In Fig. 3 c) we investigate the dependence of the lifetime on the coupling strength $c_{TB}$ for low temperature and $U = 8$ mV. From the rate equations we find simply that $T_1$ time decreases proportional to $1/c_{TB}$. But the solution of the full quantum master equation yields different results. In the considered regime excitations to the $|\Psi_{0+}^\pm\rangle$ and $|\Psi_{0-}^\pm\rangle$ play a role. The coherence leading to these superposition states is increasingly destroyed with growing coupling strength. As a result the stronger couplings even stabilizes the system by decoupling the two sides of the parabola.
FIG. 4. Relaxation time $T_1$ and decoherence time $T_2$ of the two ground states versus the applied voltage $U$ in a weak magnetic field $B_z = 10^{-8} \text{T}$ at $T = 0.7 \text{K}$ for the full master equation solution and the rate equation (12) with the $H_{C,F}$ eigenstates. a) With and without modulation voltage $U_{\text{mod}} = 0.8 \text{mV}$. b) With and without tip distance correction. For comparison the experimental data are shown in red. The error bars are too small to be visible.

FIG. 5. a) Relaxation time $T_1$ versus the bulk electron scattering strength $c_{BB}$ for the full master equation solution and the rate equation (12) based on the $H_{C,F}$ eigenstates. The parameters are $U = 5 \text{mV}$, $B_z = 10^{-8} \text{T}$, $c_{BF} = 8.53 \cdot 10^5 (\text{meV s})^{-1}$. b) Relaxation time $T_1$ versus the voltage $U$ for the model with modulation voltage broadening and tip distance correction with and without bulk electron scattering strength $c_{BB} = 3.2 \cdot 10^6 (\text{meV s})^{-1}$.

**B. Further details of the experiments**

To compare with the experiments of Ref. [1], two further effects have to be taken into account. First, in the experiment a modulation voltage of $U_{\text{mod}} = 0.8 \text{mV}$ was applied, i.e. $U_{\text{tot}}(t) = U + \sqrt{2}U_{\text{mod}} \cos(\omega t)$. The frequency of the modulation, $\omega = 720 \text{Hz}$, is several orders of magnitude faster than the timescales of interest. We model this fast oscillation by suitably averaging the correlation functions with the distribution $h(U') = 1/\pi [2(eU_{\text{mod}})^2 - (eU')^2]^{-1/2}$ for $|U'| \leq \sqrt{2}U_{\text{mod}}$ and $h(U') = 0$ otherwise [12]. This means, e.g.

$$
\tilde{C}^{TB}(\pm \Lambda_{nm}) = c_{TB} \frac{1}{2} (1 + \eta)
\int dU' \zeta(\pm \Lambda_{nm} + eU' + eU')h(U'),
$$

(14)

and respectively for all correlation functions with $\alpha \neq \alpha'$. The effect on the lifetimes is shown in Fig. 4 a). In essence, the modulation amounts to a shift $U \rightarrow U + \sqrt{2}U_{\text{mod}}$, by approximately $1.1 \text{mV}$. 
Second, in the experiment the voltage-induced tunnel current was measured, and in fact, by adjusting the distances between tip and electrode, was kept fixed at the value $I_{\text{exp}} = 1 \text{nA}$. To keep the current fixed for different voltages $U$, we allow in the simulations $c_{T_B}(U)$ to be voltage dependent. We checked numerically that the tunnel contact behaves close to Ohmic, $I_{th} \approx U/R_{\text{run}}$. We therefore adjust the coupling $c_{T_B}(U) \propto U$ to keep the current constant. We remind that an estimated 90% of the current is leakage current. With $c_{T_B}(U = 3 \text{ mV}) = 8.53 \cdot 10^5(\text{meV s})^{-1}$ we arrive at $I_{th} = 0.1 \text{nA}$. We will proceed using these values in all simulations reported below. All this being said and done, we note that the effect of the adjustment, which is included in Fig. 4(b), is weak.

V. DEVIATIONS FROM THE IDEAL SITUATION

When comparing the calculated $T_1$ times with the experimental data, as illustrated in Figs. 3, we note that the theory produces far too long times. Therefore, we need to take a closer look at the experiment and possible deviations from the ideal situation assumed so far.

A. Scattering of bulk electrons

Up to now we ignored the effect of bulk electrons scattering from the Ho atom, and the question arises whether it could be the source of the mismatch between theory and experiment. The scattering processes are easily included in the quantum master equation, and their effects are illustrated in Fig. 6. In the first panel we show how the relaxation time depends on the coupling strength $c_{BB}$ for a fixed value of the tunneling strength $c_{TB} = 8.53 \cdot 10^5(\text{meV s})^{-1}$ and voltage $U = 5 \text{ mV}$. As long as $c_{BB}$ is smaller than $c_{TB}$ the lifetime remains nearly unchanged. For stronger $c_{BB}$, the scattering of bulk electrons leads to suppression of coherent transitions and thus to longer lifetimes. This arises because of the low temperature of the bulk electrodes, which cools the system into the ground states, whereas the tunneling electrons due to the applied voltage have enough energy to excite the system. The combination of voltage-dependent tunneling and voltage independent scattering is illustrated in Fig. 6(b) (including the effects of modulation voltage broadening and tip distance correction mentioned before). We assumed a bulk electron scattering strength of $c_{BB} = 3.2 \cdot 10^6(\text{meV s})^{-1}$ which is slightly larger than the tip coupling strength $c_{TB} = 8.53 \cdot 10^5(\text{meV s})^{-1}$. Again we note the increase of the lifetime due to the scattering.

B. Breaking the $C_{3v}$-symmetry

We start considering the effect of the leading $C_{3v}$-symmetry-breaking term of the Stevens operators, $H_{SB} = B_{2}^{1} \cdot O_{\frac{1}{2}}^{1} = B_{2}^{1} \cdot [J_{z}, J_{+} + J_{-}]_{+}$. This term arises if the tip is not perfectly centered over the Ho atom, or if nearby surfaces or imperfections in the crystal break the symmetry. A magnetic field in the xy-plane would have a similar effect.

The symmetry-breaking parameter $B_{2}^{1}$ is varied in Fig. 6(a) between $10^{-10} \text{meV}$ and $10^{-8} \text{meV}$, which is still orders of magnitude lower than the leading crystal field term $B_{2}^{0} = -0.239 \text{meV}$. As a result of the symmetry breaking, the eigenstates of $H_{CF}$ get mixed, and the protection against direct transitions is lost. In Fig.
a), the voltage is chosen to be $U = 5$ meV, so the leading transition is directly between the two ground states. With rising strength of $B_3^2$ the relaxation time decreases $T_1 \propto (B_3^2)^{-2}$. The switching as obtained from the rate equations arises since electron tunneling directly couples the two states. In the frame of the full master equation scattering of electrons destroys the phase coherence of these superpositions and the resulting $J_z$ expectation values of the steady states are closer to the parabola characteristic for the ideal $H_{CF}$ eigenbasis (see the ground states of the inset of Fig. 6(a)). This results in a longer relaxation time $T_1$. Unfortunately, the parameter $B_3^2$ is not independently accessible in the experiment, and therefore it is difficult to draw more precise conclusions.

C. Noise in the circuit

To account for the influence of further perturbations, such as thermal noise in the electronics, we introduce a lifetime broadening. Specifically we average the results obtained so far, assuming a Gaussian broadening of the tunneling electron energy distribution $g(dE, G) = 1/(\sqrt{2\pi}G^2) \exp[-dE^2/(2G^2)]$ with a width characterized by the parameter $G$ [18]. Its influence on the lifetime $T_1$ is visualized in Fig. 6(b). The relaxation is strongly reduced by this broadening because it allows exciting the system into one of the $|\Psi^+_g\rangle$ or $|\Psi^-_g\rangle$ states, followed by a subsequent decay to the other ground state.

By fitting the parameters characterizing the two deviations from the ideal situation we manage to obtain results for the $T_1$ times close to the the experimental ones (see Fig. 7). We plot results for two values of the temperature $T = 0.7$ K and $T = 1.4$ K, where the first one is the bath temperature in the experiment while the second is chosen to account for some electron heating induced by the current. (By itself the higher temperature would not be sufficient to explain the discrepancy between the simulation based on the ideal model and the experiment.) Although with the fitting we have reached a reasonable agreement with experiment we have to note that the fit is not conclusive, since the number of data points is too low to determine the parameters independently.

D. Magnetic field dependence

Next, we investigate the effect of an applied or stray magnetic field $B_z$ which is probably present in experiments. Its influence depends strongly on the values of the other parameters. In Fig. 8(a) we show the resulting modification for the regime where the main transition, although with small rate, is directly between the states $|\Psi^+_g\rangle$ and $|\Psi^-_g\rangle$. We choose $U = 5$ mV, i.e., we are still in the regime of voltage-independent relaxation time of Fig. 6(a). As shown in Fig. 8(a) the lifetime is strongly reduced by the symmetry breaking magnetic field $B_z$, since the symmetry protection of the two ground states is lost.

This behavior is obtained both from the rate equation and the solution of the quantum master equation.

Interestingly, as illustrated by Fig. 8(b), the behavior can be completely different for different parameters. In this example the lifetime increases when a field is applied. For the chosen parameters the $B_z$ field stabilizes the $J_z$ eigenstates and reduces the switching, which otherwise would be induced by the symmetry breaking term $B_3^2$. We conclude that a detailed study of the magnetic field dependence could provide a better understanding of the different perturbations acting on the Ho adatom.

E. Alternative choice of $H_{CF}$

In a recent publication Donati et al. [6] reported about x-ray absorption spectroscopy (XAS) and magnetic circular dichroism (XMCD) measurements performed with Ho on Pt(111). The results could be fitted with a crystal field Hamiltonian containing only the terms $B_3^2 = -140 \mu$eV and $B_3^4 = 1 \mu$eV, which differs drastically from what Miyamachi et al. [1] used, and what we assumed so far in this paper. We add a small $B_3^4 \approx 0.3 \mu$eV which we take from Miyamachi et al. [1] because otherwise the ground states decouple completely. With these inputs, we arrive at the level scheme shown in the inset of Fig. 9. Most important we note that the ground states are the $|\Psi_{gs}^0\rangle$ and $|\Psi_{gs}^0\rangle$, which are much stronger coupled (not symmetry-protected) than the states $|\Psi^+_g\rangle$ and $|\Psi^-_g\rangle$ and

![Figure 7](image-url)
from the rate equations (12) based on \( H_{CF} \) eigenstates. The insets show the expectation value of \( J_z \) for the two descriptions. a) Results for the ideal model for \( T = 0 \) K, \( c F \) = 0.8 mV, \( G = 0.95 \) meV, and \( B_z = 4 \cdot 10^{-3} \) meV.

The decoherence time \( T_2 \)

The decoherence time \( T_2 \) is the time scale on which the phase information in a coherent superposition, here specifically of the states \( |\Psi_0^+\rangle \) and \( |\Psi_0^-\rangle \), gets lost. In the quantum master equation treatment of the problem \( T_2 \) is obtained from the decay rate of the off-diagonal matrix element \( \rho_{+,-}\simeq \), which is given by the corresponding matrix element in the matrix \( M \),

\[
1/T_2 = - M_{+,-}\simeq \langle \Psi_0^+|J_z|\Psi_0^-\rangle \zeta(eU) \\
\approx - 1024 c_{TB} eU. \quad (15)
\]

The resulting \( T_2 \) times are plotted for different parameters in Figs. 6, 8 and 9. It turns out that the \( T_2 \) time depends mostly on the current, i.e., on the number of scattered electrons. Each scattered electron dephases the
superposition state, independent of the energy of the electron. Thus, we detect only in Fig. 3 a) and Fig. 4 a) a dependence of $T_2$ on the voltage $U$, because in all other plots the current is kept constant (achieved by adjusting $c_{TB}(U)$). We note that the $T_2$ times are always very short ($\sim 10^{-10} \text{s}$) making the considered memory unsuitable as a quantum mechanical bit (qubit). Additionally, we found that the $T_2$ does not depend on the symmetry breaking $B_z$, the broadening $G$, or the magnetic field $B_z$.

VII. INITIALIZATION

We have seen that the relaxation time depends strongly on various parameters. In this section we will demonstrate that by switching parameters in a suitable way we can initialize a specific angular momentum state. This allows the writing process if we use the Ho atom as a memory. As a specific example we study what happens to the state $|\Psi_{-s}\rangle$ when we pulse the system for a time $t_p$ with a voltage $U$ and then let the system relax for $1 \mu$s without a voltage applied. After the relaxation, the population of the state $|\Psi_s^p\rangle$ is measured, which provides the information about the switching probability $S_{-s\rightarrow s}(U, t_p)$.

In Fig. 10 the switching probability $S_{-s\rightarrow s}(U, t_p)$ as obtained from the quantum master equation is plotted versus the strength of the applied voltage pulse for different spin polarizations $\eta$ of the tip. (We neglect again the influence of the bulk electron scattering.) For $U > 20 \text{ mV}$ the value of $S_{-s\rightarrow s}(U, t_p)$ may get close to $1$, i.e., the pulse flips the Ho atom with a high probability into the $|\Psi_s^p\rangle$ state. On the other hand, a pulse with opposite voltage $U < -20 \text{ mV}$ leaves the state with high probability in the $|\Psi_{-s}\rangle$ state. For voltages between $-10 \text{ mV} \lesssim U \lesssim 10 \text{ mV}$ basically no switching Ho spin state is induced, $S_{-s\rightarrow s}(U, t_p) \approx 0$. Around $U = 20 \text{ mV}$ the switching is strongest as long as $\eta \neq 0$. For an unpolarized tip, $\eta = 0$, a pulse with high voltage produces a balanced population of the two ground states.

The upper inset of Fig. 10 shows the dependence of the switching probability $S_{-s\rightarrow s}(U, t_p)$ on the spin polarization $\eta$ for optimum conditions $U = 20 \text{ mV}$ and pulse time $t_p = 2.5 \cdot 10^{-7} \text{s}$. As one could expect, the higher the polarization, the better the initialization. But, the switching between the ground states also requires a certain number of electrons, which increases with longer pulse time $t_p$, as displayed in the lower inset of Fig. 10. For the optimal voltage of $U = 20 \text{ mV}$ we calculate a current of $I_{TH} \approx 0.7 \text{nA}$. A pulse time of $t_p \approx 250 \text{ ns}$ implies then that around 1000 electrons are needed to prepare the atom in one state. By changing the tip distance in the experiment, this dependence could be probed.

Our simulations suggest that by the considered protocol it is possible to prepare the system in a required state using pulse times of a few hundreds nanoseconds with high fidelity as long as the tip polarization is good enough. The required pulse time depends strongly on the parameter $c_{TB}$. Thus, an experiment with different pulse lengths could help to determine the value of $c_{TB}$.

VIII. CONCLUSION

When investigating the dynamics of the angular momentum states of Ho on Pt(111) we found that in an important regime of parameters the system behaves deeply quantum mechanically and cannot be described by a rate equation for transitions between the eigenstates of the crystal field Hamiltonian $H_{CF}$. Rather the system has to be treated by the full quantum master equation. Its steady-state basis in general differs from the $H_{CF}$ eigenstates, which is an example of the “environment-induced superselection” principle. We analyzed how the relaxation time depends on various parameters of the system which allows us, by comparing with experiment, to estimate their values. We further described a method to initialize the system in one of the two ground states by suitable voltage pulses. This models the writing process of a memory bit.

Our analysis shows that if the parameters could be controlled more precisely and could be improved the system would acquire even longer lifetimes than observed already. The system therefore promises to be useful as a single-atom memory device with the possibility to write into the memory by very short pulses of electric currents with high fidelity. A further detailed investigation of the coupling parameter $c_{TB}$ and the other parameters is required to identify the main perturbation which limits the lifetime of the Ho adatom in the experiment. A magnetic field analysis could be a first important step to obtain the missing information, because of the strong
dependence of the lifetime on this parameter.

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Appendix A: Stevens operators and parameters

For convenience we list here the Stevens operators which are needed to describe the system $H_0$ on Pt(111) 

$$O_0^0 = 3J_z^2 - J(J + 1),$$
$$O_0^1 = 35J_z^5 - 30J(J + 1)J_z^2 + 25J_z^2 - 6J(J + 1)$$
$$+ 3J^2(J + 1)^2,$$  \( \text{(A1)} \)
$$O_0^2 = \frac{1}{4} \left[ J_z(J_z^3 + J_z^3) + (J_z^3 + J_z^3)J_z \right],$$  \( \text{(A2)} \)
$$O_0^3 = 23J_z^6 - 315J(J + 1)J_z^4$$
$$+ 735J_z^2 + 105J^2(J + 1)^2J_z^2$$
$$- 525J(J + 1)J_z^2$$
$$+ 294J_z^2 - 5J(J + 1)^3 +$$
$$40J^2(J + 1) - 60J(J + 1),$$  \( \text{(A3)} \)
$$O_0^4 = \frac{1}{4} \left[ (11J_z^3 - 3J(J + 1)J_z - 59J_z)(J_z^3 + J_z^3) $$
$$+ (J_z^3 + J_z^3)(11J_z^3 - 3J(J + 1)J_z - 59J_z) \right],$$  \( \text{(A4)} \)
$$O_0^5 = \frac{1}{2} \left[ J_z^6 + J_z^6 \right].$$  \( \text{(A5)} \)

We also list the parameters which were obtained from ab-initio simulations and listed in Ref. 1.

| Anisotropy constant | value |
|---------------------|-------|
| $B_2$               | -239 µeV |
| $B_3$               | 86 neV |
| $B_4$               | 293 neV |
| $B_6$               | 0.186 neV |
| $B_7$               | 0.967 neV |
| $B_8$               | 0.630 neV |

**TABLE I. Calculated anisotropy parameters.**

Appendix B: Setting up the matrix $M$

In this section we present the approach we use to solve the quantum master equation in Born-Markov approximation. By using the explicit time dependence of the system operators $J_x(t)$ in the interaction picture we evaluate the time integrals including the correlation functions of the master equation \([21,22]\)

$$S^{\alpha \alpha'}_{\nu \nu'}(\pm \tau) \equiv \int_0^\infty d\tau C^{\alpha \alpha'}_{\nu \nu'}(\pm \tau)e^{-H_S \tau}J_\nu e^{iH_S \tau}. \quad \text{(B1)}$$

In the eigenbasis of $H_S |n\rangle = E_n |n\rangle$, the matrix elements of $S^{\alpha \alpha'}_{\nu \nu'}(\pm \tau)$ become

$$\langle n | S^{\alpha \alpha'}_{\nu \nu'}(\pm \tau) | m \rangle = \int_0^\infty d\tau C^{\alpha \alpha'}_{\nu \nu'}(\pm \tau)$$

$$\langle n | e^{-H_S \tau} | n \rangle \langle J_\nu | m \rangle \langle m | e^{iH_S \tau} | m \rangle$$

$$= \langle n | J_\nu | m \rangle \int_0^\infty d\tau C^{\alpha \alpha'}_{\nu \nu'}(\pm \tau)e^{iA_{nm}\tau} \quad \text{(B2)}$$

$$= \langle n | J_\nu | m \rangle \int_0^\infty d\tau C^{\alpha \alpha'}_{\nu \nu'}(\pm \tau)$$

$$\int_0^\infty d\omega \tilde{C}^{\alpha \alpha'}_{\nu \nu'}(\pm \Lambda_{nn}) - i P \int d\omega \frac{\tilde{C}^{\alpha \alpha'}_{\nu \nu'}(\pm \omega)}{\Lambda_{nn} \pm \omega}. \quad \text{(B3)}$$

Here, $\Lambda_{nm} = E_m - E_n$ are the energy differences and the tilde over the correlation functions indicate Fourier transforms. The imaginary parts of this equation vanish in the Born-Markov approximation because in the master equation complex conjugate terms are summed. The prefactor $\sqrt{\pi}$ rescales the parameters $c_{TB}$ and $c_{EB}$. For a formulation that can be implemented efficiently in source code, the quantum master equation is rewritten in the form

$$\frac{d}{dt}\vec{\rho} = M\vec{\rho}. \quad \text{(B5)}$$

Here $\vec{\rho} = \text{vec}\{\rho\}$ denotes the column-vectorization of the matrix $\rho$, meaning that the $(i+1)^{th}$ column of the matrix is written below the other $i$ ones. The supermatrix $M$ has the dimension $\text{dim}(\rho)^2$, which implies an extension of the complexity, but on the other hand the solution of this equation is possible with standard numerical tools. With the help of the relation \([22]\)

$$\text{vec}\{AXB\} = (A \otimes B^T)\text{vec}\{X\}, \quad \text{(B6)}$$

where $A$, $X$ and $B$ are matrices, the transformation of quantum master equation \([3]\) into the wanted type is possible. The symbol $\otimes$ is the Kronecker-product of the matrices is defined as

$$A \otimes B = \begin{bmatrix} a_{11}B & \cdots & a_{1m}B \\ \vdots & \ddots & \vdots \\ a_{m1}B & \cdots & a_{mn}B \end{bmatrix}. \quad \text{(B7)}$$

For the problem considered in this paper we get

$$M = M_C + M_D \quad \text{(B8)}$$

$$M_C = i(1 \otimes H_S^T - H_S \otimes 1) \quad \text{(B9)}$$

$$M_D = - \sum_{\nu,\nu' = -1,0,1} \left[ J_{\nu'} S^{\alpha \alpha'}_{\nu \nu'}(+\tau) \otimes 1 \right] + \left( 1 \otimes S^{\alpha \alpha'}_{\nu \nu'}(-\tau)J_{\nu}^T \right) + \left( 1 \otimes S^{\alpha \alpha'}_{\nu \nu'}(-\tau)J_{\nu}^T \right)$$

$$\left( 1 \otimes S^{\alpha \alpha'}_{\nu \nu'}(-\tau)J_{\nu}^T \right) - \left( J_{\nu} \otimes [S^{\alpha \alpha'}_{\nu \nu'}(-\tau)]^T \right), \quad \text{(B10)}$$

where $M_C$ contains the coherent part of the master equation and $M_D$ the dissipative part.
Appendix C: Calculating the Current

The current is given by the time-derivative of the number of particles of the tip \(N_T(t) = \sum_{k\sigma} c_{k\sigma}^T(t) c_{k\sigma}^\dagger(t)\),

\[
I_{Th}(t) = e \frac{d}{dt}(N_T(t)) = ie\langle[H, N_T](t)\rangle. \tag{C1}
\]

In the commutator \([H, N_T](t)\) only the coupling Hamiltonian \(H_C\) survives, which leads to

\[
I_{Th}(t) = -ie \sum_{kk'} t^{TB} \left( \langle J_+ c_{k\uparrow}^B c_{k'\uparrow}^\dagger(t) \rangle + \langle J_- c_{k\uparrow}^B c_{k'\uparrow}^\dagger(t) \rangle \right) \\
+ \langle 2J_z \left[ c_{k\uparrow}^B c_{k'\uparrow}^\dagger(t) - c_{k\downarrow}^B c_{k'\downarrow}^\dagger(t) \right] \rangle \\
- \langle J_+ c_{k\downarrow}^B c_{k'\uparrow}^\dagger(t) \rangle - \langle J_- c_{k\uparrow}^B c_{k'\downarrow}^\dagger(t) \rangle \\
- \langle 2J_z \left[ c_{k\downarrow}^B c_{k'\uparrow}^\dagger(t) - c_{k\uparrow}^B c_{k'\downarrow}^\dagger(t) \right] \rangle. \tag{C2}
\]

This form of the current bears similarity to terms in the master equation. It contains all the tunneling events from the tip to the bulk with a positive sign and those in opposite direction with a negative sign. Proceeding similar to the steps used for the dissipative part \(M_D\) of the master equation in Born-Markov approximation, and concentrating on the stationary limit one finds \[23\]

\[
M_D^I = \sum_{\nu,\nu'} \left( [S_{\nu\nu'}^{TB}(+\tau) \otimes (J_\nu)^T] + (J_\nu \otimes [S_{\nu\nu'}^{TB}(-\tau)]^T) \\
- (S_{\nu\nu'}^{BT}(+\tau) \otimes (J_\nu)^T) - (J_\nu \otimes [S_{\nu\nu'}^{BT}(-\tau)]^T) \right), \tag{C3}
\]

\[
I_{Th} = \text{Tr}\left[ \hat{I}_{Th}\rho \right] = e \sum_{ij} (M_D^I)_{(j-1)i,17+i} \langle \hat{\rho}_{St} \rangle_i. \tag{C4}
\]

The sum over \(j\) runs over all states, \(1 \leq j \leq 17\), whereas the sum over \(i\) is also over all off-diagonal elements, thus \(1 \leq i \leq 17^2 = 289\). The complicated indices of \(M_D^I\) in the sum are a result of the vectorization of the trace.

To estimate the 'leakage' current \(I_{Leak}\) mentioned in the main part of the paper we use the fact that the leakage current does not depend on the state of the Ho atom and thus can be distinguished from \(I_{Th}\). By measuring the step from elastic to inelastic current for energies below and above the first excitation gap in the \(dI/dV\) curve, the leakage current can be determined. The step size is defined as

\[
s = \frac{\frac{dI}{dV}(U > \Delta E_{87})}{\frac{dI}{dV}(U < \Delta E_{87})} - 1. \tag{C5}
\]

In the experiment, a step of \(s_{Exp} \approx 0.2\%\) was measured. In the theory without any broadenings and modulation we find \(s_{Th} \approx 10\%\). With an optimistic estimation we assume that \(I_{Th}\) should be 10% of the total current \(I_{Exp}\) to have a better match of the step sizes.