We present a theoretical framework to evaluate the conditions and outcome of experiments directed to controlling quantum systems using electrical means. In particular, recent experiments have shown important progress in the excitation of single-atom spin resonances using a scanning tunneling microscope. Although general, we show that the theory presented here can be applied to understand the ingredients, parameters and results of such experiments. The theory is based on non-equilibrium Green’s functions that allow us to treat realistic bias drops and electron flow through an atomic system connected to two electrodes. The full quantum response of the system is obtained by doing perturbation theory in the hopping terms between the atomic system and the electrodes. Applying an electrical field changes the tunneling conditions of electrons. We suggest this mechanism to explain the process of driving an atomic spin with a time-dependent electrical field. The tunneling barrier is modulated by the time-dependent field and this leads to a time-dependent hopping matrix element between the quantum system and the electrodes. An electron that enters the impurity or atomic site is coupled to the rest of the spin of the system via a magnetic exchange interaction. This is equivalent to a Kondo Hamiltonian that takes into account the exchange coupling between electrons and spins in the atomic system. We apply this theory to two cases. The simplest case is just a single atomic orbital subjected to a time-dependent electric field, and the second case consist of a single atomic orbital coupled to a second spin-1/2 under the same type of driving as before. The first case already reproduces the main experimental features Ti atoms on MgO/Ag (100) while the second one directly addresses the experiments on two Ti atoms. These calculations permit us to explore the effect of different parameters in the driving of the spins as well as to reproduce experimental fingerprints.

I. INTRODUCTION

Electron transport on the atomic scale has experienced a fast evolution in the last two decades both experimentally [1] and theoretically [2]. The development of scanning probes together with break junctions has permitted us to have controlled atomic devices that have explored non-equilibrium electron transport and open venues for the creation of new technologies [3]. Most studies have considered electronic currents in the stationary limit and the effect of time-dependent electron sources on the transport problem has seen a smaller development. The use of time-dependent currents can have very interesting applications, particularly in the presence of atomic excitations. When the excitations are magnetic, different regimes can exist, giving rise to the possibility of driving a few-level system with a passing electronic current in a controlled way. For these reasons, it is of fundamental interest to understand how electronic currents interact with magnetic degrees of freedom under time-dependent driving.

An application of magnetic time-dependent driving is electron spin resonance (ESR). ESR is a very well-established analysis tool [4] routinely applied to a variety of fields such as medicine, chemistry and engineering. Standard ESR is an ensemble technique [5] with typical commercial devices requiring samples as small as 100 µm$^3$. Recent STM studies [6, 7] have pushed ESR to the atomic limit, providing us with a new experimental method capable of spatial atomic resolution and nano-eV-energy resolution. This was possible thanks to inte-
We use the Schwinger-Keldysh formalism to describe a quantum few-level system (quantum dot, atom or molecule, from now on the quantum impurity, QI). The full quantum dynamics of the combined system is derived by using perturbation theory on the coupling between impurity and reservoirs to calculate the evolution of the reduced density matrix on the impurity’s degrees of freedom. Under these conditions, a time-dependent quantum master equation can be written. The master equation is then solved using Floquet’s theory for time-dependent linear equations. The impurity is taken as an electron orbital with a large Coulomb repulsion \( U \) (we focus on the \( U \rightarrow \infty \) limit) that is coupled to the reservoirs via tunneling hoppings matrix elements, \( w_L \) and \( w_R \). In this way, transport takes place through the impurity. A spin-1/2 system is of little interest for quantum dynamics. In order to have a more interesting system, we consider an impurity with an extra local spin \( S \) as in the case of atomic systems with several filled orbitals and a Hund rule. When the external orbital is occupied by a single electron, its spin interacts with the local one via a magnetic exchange coupling \( J \). This is very similar to the \( sd \) or Kondo Hamiltonian where the electron causing the spin coupling is actually being transferred between reservoirs. Due to the followed perturbative approach, we can treat spin fluctuations but at the lowest-order in the tunneling process and so called Kondo effect is then absent from this work. Figure 1 shows a scheme of the system treated here. Despite its apparent simplicity, the presence of the magnetic exchange coupling leads to a very rich situation in which we can take into account the physics leading to the experimental results of STM-ESR measurements.

The present article is mainly devoted to presenting the theoretical approach to solve the above problem. Given the connections to quantum control and quantum operations, we think it is of utmost interest to find new theoretical frameworks and solution techniques to tackle these problems. As illustration, we choose an impurity system coupled to two free-electron electrodes that is first uncoupled to a spectator spin \( (S = 0) \) and in a second case, to another spin-1/2 system \( (S = 1/2) \) such that the first case can be used to study the driving of a spin-1/2 system and the second case can be used for a spin-1 system. To simplify the calculations, we have chosen symmetric couplings to the electrodes such that the bias drops symmetrically in the junction. As in STM-ESR experiments, the periodic driving is performed using a bias voltage \( V(t) = V_{AC} \cos(\omega t) + V_{DC} \), where \( V_{AC} \) and \( V_{DC} \) are constant and they represent the periodic bias amplitude and the continuous or DC one. The driving frequency is \( \omega/2\pi \).

The results presented in this work are all in the sequential tunneling regime, where the impurity orbital is assumed to be within the DC bias window and the couplings small enough to describe the electron transport as a sequential set of single-electron transfers in and out of the impurity. This situation is not the usual one in STM-ESR, where the impurity’s orbital lies out of the...
II. THEORETICAL APPROACH

A. Model

The quantum system we study consists of a quantum magnetic impurity tunnel-coupled to two electron reservoirs, see Fig. 1. We model the impurity’s internal structure by a local quantum spin \( S \) exchange-coupled to the spin of an electron trapped in a single external orbital of the impurity. This single orbital is itself hybridized with the left and right electrodes. Full system is described by the following Hamiltonian,

\[
H(t) = H_{\text{res}} + H_T(t) + H_{\text{impurity}},
\]

where the first term describes the reservoirs modeled by free electron gases

\[
H_{\text{res}} = \sum_{\alpha k \sigma} \varepsilon_{\alpha k} c_{\alpha k \sigma}^\dagger c_{\alpha k \sigma},
\]

Here, \( \alpha \) identifies the electrode (\( \alpha = \text{L, R} \)), while \( \sigma = \uparrow, \downarrow \) is the electron spin projection along the quantization axis. These two systems have temperatures and chemical potentials \( T_\alpha, \mu_\alpha \). The impurity is modeled by the following Hamiltonian

\[
H_{\text{impurity}} = \sum_{\sigma} \varepsilon_{\sigma} d_{\sigma}^\dagger d_{\sigma} + J \hat{S} \cdot \hat{s} + D (\hat{S}_z + \hat{s}_z)^2 + U \hat{n}_{d \uparrow} \hat{n}_{d \downarrow} + H_{\text{Zeeman}},
\]

where \( \varepsilon_\sigma = \varepsilon \) is the energy of the localized electronic state, \( U \) is the corresponding Coulomb repulsion, and \( \hat{n}_{d \sigma} = d_{\sigma}^\dagger d_{\sigma} \) is the occupation operator of the localized state. The localized electrons of the internal orbitals are represented by the spin operator \( \hat{\mathbf{S}} \). The second term describes the magnetic exchange with strength \( J \) between the conduction electrons with spin \( \hat{\mathbf{s}} \) and the localized spin \( \hat{\mathbf{S}} \). The spin operator for the electrons on the single orbital has components \( \hat{s}_i = \sum_{\sigma \sigma'} \hat{\sigma}_{\sigma \sigma'} d_{\sigma}^\dagger d_{\sigma'}, \) being \( \hat{\sigma}_{\sigma \sigma'} \) \( j = x, y, z \) Pauli matrices. Here \( D \) is the anisotropy parameter, which is assumed to act on the total spin, higher orders in the anisotropy can be easily included. For a review on spin Hamiltonians see for example Ref. 39. The last term of Eq. (3) represents the Zeeman interaction between the total spin of the impurity \( \hat{S}_T = \hat{\mathbf{S}} + \hat{\mathbf{s}} \) and an external uniform magnetic field \( \mathbf{B} \), which reads as

\[
H_{\text{Zeeman}} = g \mu_B \mathbf{B} \cdot (\hat{\mathbf{S}} + \hat{\mathbf{s}}).
\]

The tunnel-coupling between the impurity and the two reservoirs is described by the Hamiltonian

\[
H_T(t) = \sum_{\alpha k \sigma} \left( w_\alpha(t) c_{\alpha k \sigma}^\dagger d_{\sigma} + w_\alpha^*(t) d_{\sigma}^\dagger c_{\alpha k \sigma} \right).
\]

In the present treatment, the driving is produced by the action of the electrical field on the hopping terms, \( w_\alpha(t) \). For low-enough drivings, we can use a Taylor expansion.
on the applied bias, $V(t) = V_{DC} + V_{AC} \cos(\omega t)$, to write the time-dependent hopping as

$$w_\alpha(t) = w_\alpha^0 |C_\alpha + A_\alpha \cos(\omega t)|,$$

where $A_\alpha \propto V_{AC}$ is the quantity that reflects the driving per electrode and $C_\alpha$ is meant to simulate the piezoelectric effect present in the experiments. Since we want to remain as simple as possible, we set $C_\alpha = 1$. The actual value of the driving amplitude $A_\alpha$ depends on the modulation of the tunneling amplitude by the applied bias. Using a WKB approach, one obtains $A_\alpha$ ranging from $10^{-3}$ to $0.5$ for the typical STM-ESR experimental conditions [35].

We focus on the limit of $U \to \infty$ in Eq. (3), which corresponds to the situation where the external orbital can be only empty or singly occupied. In such a case, it is convenient to introduce the basis $|p, m\rangle$, where the first entry $p = 0, \uparrow, \downarrow$ corresponds to the state of the conduction orbital while the second one corresponds the magnetic quantum number $m = -S, \ldots, S$ associated to the localized spin. The Hamiltonian for the impurity defined in Eqs. (3), in the limit of vanishing double occupation, can be written as

$$H_S = \sum_{p,m} \varepsilon_{pm} |p, m\rangle \langle p, m| + H_{\text{Zeeman}}$$

$$+ \sum_m \left( J_m |\downarrow, m+1\rangle \langle \uparrow, m| + \text{h.c.} \right),$$

(7)

where we have introduced the definitions

$$\varepsilon_{pm} = \delta_{p,\sigma} \left[ \varepsilon + Jm \frac{s_\sigma}{2} + D \left( \frac{1}{4} + ms_\sigma \right) \right] + Dm^2,$$

$$J_m = \frac{J}{2} \sqrt{S(S+1) - m(m+1)},$$

(8)

with $s_\uparrow = +1$ ($s_\downarrow = -1$). The corresponding tunneling Hamiltonian expressed in this basis reads

$$H_T'(t) = \sum_{a, \alpha, m} \left( w_\alpha(t) c^\dagger_{a, \alpha, m} |0, m\rangle \langle \sigma, m| + \text{h.c.} \right).$$

(9)

It is convenient to express the Hamiltonian for the impurity and the tunneling coupling in the basis of eigenstates of the Hamiltonian defined in Eq. (7), $H_S |\ell\rangle = E_\ell |\ell\rangle$, $\ell = 1, \ldots, 3(2S+1)$. Accordingly, $H_T'(t)$ is written as follows

$$H_T'(t) = \sum_{a, \alpha, \sigma, \ell j} \left( w_\alpha(t) c^\dagger_{a, \alpha, \ell j} \lambda_{\ell j, \sigma} |j\rangle \langle \ell | + \text{h.c.} \right),$$

(10)

with

$$\lambda_{\ell j, \sigma} = \sum_m \langle l | 0, m \rangle \langle \sigma, m | j \rangle.$$  

(11)

Notice that the Hamiltonian of Eq. (7) commutes with the particle-number operator for the external orbital, $\hat{n}_d = \sum_\sigma d^\dagger_\sigma d_\sigma$. Hence, the states $|\ell\rangle$ are states with a well defined occupancy number $n_d = 0, 1$. The total spin of the isolated impurity for $B = D = 0$, is a good quantum number, which takes values $S_T = S \pm 1/2$, for $S > 0$ and $S_T = 1/2$ for $S = 0$, in the configuration with $n_d = 1$.

B. Derivation of the Floquet master equation

We proceed similarly to Refs. [10, 46] to derive the quantum master equation by treating the coupling between the impurity and the reservoirs at the lowest order in perturbation theory, in the framework of nonequilibrium Green's function formalism. First, we take into account that any operator $O$ acting on the Hilbert space of the impurity can be written as

$$O = \sum_{l,j} O_{lj} \hat{\rho}_{lj},$$

(12)

where $O_{lj} = \langle l | O | j \rangle$ are the matrix elements of the operator $O$ in the basis of eigenstates of $H_S$. Therefore, the corresponding average value at a given time $t$ can be written as follows,

$$\langle O \rangle(t) = \text{Tr} [\hat{\rho}_T(t) O(t)] = \sum_{l,j} O_{lj}(t) \rho_{lj}(t).$$

(13)

We have introduced the definition of the elements of the reduced density matrix,

$$\rho_{lj}(t) = \text{Tr} [\hat{\rho}_T(t) \hat{\rho}_{lj}],$$

(14)

with the trace taken over the degrees of freedom of the total system including the impurity, the reservoirs and the couplings between them. In the present problem $\hat{\rho}_{lj} = |l\rangle \langle j|$ resemble the so-called Hubbard operators [47] and are defined for any pair $|l\rangle$, $|j\rangle$ of many-body eigenstates of the Hamiltonian $H_S$. Our goal is the derivation of the equation ruling the dynamics of $\rho_{lj}(t)$. Changing to the Heisenberg picture with respect to the full Hamiltonian, we can write $\rho_{lj}(t) = \text{Tr} [\hat{\rho}_0 \hat{\rho}^H_{lj}(t)]$ with $\hat{\rho}^H_{lj}(t) = U(t, t_0) \hat{\rho}_{lj} U^\dagger(t, t_0)$ being $\hat{\rho}_0$ the density matrix at the initial time $t_0$ and $U(t, t_0) = \hat{T} \left[ e^{-i \int_{t_0}^t dt' H(t')/\hbar} \right]$ the evolution operator with $\hat{T}$ the time-ordering operator. The upper indices “$H$” indicate that the operator is expressed in the Heisenberg picture with respect to the Hamiltonian $H$. The equation of motion for $\rho_{lj}(t)$ is
where we have used the property $\hat{\rho}_{uv} \hat{\rho}_{ij} = \hat{\rho}_{ij} \delta_{uv}$ and we have introduced the definitions of the lesser Green’s functions

$$ G^{<}_{\nu,\nu}(t, t') = \pm i \langle \hat{c}^\dagger_{\nu}(t') \hat{\rho}_{ij}(t) \rangle, \\
G^{<}_{\nu,\nu}(t, t') = \pm i \langle \hat{\rho}^\dagger_{ij}(t') \hat{c}_{\nu}(t) \rangle. \quad (16) $$

The upper/lower signs apply to many-body states $|l\rangle$, $|j\rangle$ of the impurity that differ in an odd/even number of fermions (we recall that the number of particles is conserved in $H_S$).

We now define the interaction picture with respect to the uncoupled Hamiltonian $\hat{h} = H_{\text{res}} + H_S$. Hence, the lesser Green’s functions for these isolated systems are given by

$$ G^{<}_{\nu,\nu}(t, t') = \pm i \langle \hat{c}^\dagger_{\nu}(t') \hat{\rho}_{ij}(t) \rangle, \\
G^{<}_{\nu,\nu}(t, t') = \pm i \langle \hat{\rho}^\dagger_{ij}(t') \hat{c}_{\nu}(t) \rangle. \quad (17) $$

The corresponding greater functions read $g^{>}_{\nu,\nu}(t, t') = \left[ g^{>}_{\nu,\nu}(t', t) \right]^\dagger$, while the retarded and advanced ones are $g^{\pm}_{\nu,\nu} = \theta(t - t') \left[ g^{>}_{\nu,\nu}(t, t') - g^{<}_{\nu,\nu}(t, t') \right]$ and $g^{\pm}_{\nu,\nu}(t, t') = \left[ g^{<}_{\nu,\nu}(t', t) \right]^\dagger$, respectively. By using the Langreth theorem in the Schwinger-Keldysh contour, at the 1st order of perturbation theory of the mixed Green’s functions,

\[
\frac{d\rho_{ij}(t)}{dt} = \frac{i}{\hbar} (E_i - E_j) \rho_{ij}(t) + \frac{1}{\hbar} \sum_{\alpha k, u, \sigma} w_{\alpha k}(t) \left[ \lambda_{u\sigma} G^{<}_{\alpha j, \alpha k}(t, t) - \lambda_{j u\sigma} G^{<}_{\alpha k, \alpha u}(t, t) \right. \\
+ \lambda_{j u\sigma} G^{<}_{\alpha k, j u}(t, t) - \lambda_{u j u\sigma} G^{<}_{\alpha k, u l}(t, t) \right], \quad (15)
\]

Eqs. [16], in $w_{\alpha}^0$—see details in Appendix A—we get the following equation

\[
\hbar \dot{\rho}_{ij}(t) - i \Delta_{ij} \rho_{ij}(t) = \sum_{\nu u} \left[ \Gamma_{\nu v, \nu u}(t) \rho_{\nu v}(t) + \tilde{\Gamma}_{\nu v, \nu u}(t) \rho_{\nu u}(t) \right. \\
- \Gamma_{\nu v, \nu u}(t) \rho_{\nu u}(t) - \tilde{\Gamma}_{\nu v, \nu u}(t) \rho_{\nu v}(t) \right], \quad (18)
\]

where the time-dependent driving entails a implicit time-dependence of the rates $\Gamma(t)$ and $\tilde{\Gamma}(t)$.

We now introduce the Fourier-Floquet representation for the time-dependent rates,

$$ \Gamma_{\nu v, \nu u}(t) = \sum_{n'} \int_{0}^{2\pi/\omega} \rho_{ij}(t) e^{-i n' \omega t} \Gamma_{\nu v, \nu u}(\omega), \\
\tilde{\Gamma}_{\nu v, \nu u}(t) = \sum_{n'} \int_{0}^{2\pi/\omega} \rho_{ij}(t) e^{-i n' \omega t} \tilde{\Gamma}_{\nu v, \nu u}(\omega). \quad (19) $$

We notice that the stationary solution of this master equation depends harmonically on time. Hence, it is appropriate to expand it as

$$ \rho_{ij}(t) = \sum_{n} e^{-i n \omega t} \rho_{ij;n}, \quad (20) $$

with

$$ \rho_{ij;n} = \frac{\omega}{2\pi} \int_{0}^{2\pi/\omega} \rho_{ij}(t) e^{i n \omega t}. \quad (21) $$

Substituting in Eq. (18), we get the Floquet master equation

\[
(E_i - E_j) \rho_{ij;n} + n \hbar \omega \rho_{ij;n} = \\
i \sum_{\nu u; n'} \left[ \Gamma_{\nu v, \nu u;n'}(\omega) \rho_{\nu u;n' - n'} + \tilde{\Gamma}_{\nu v, \nu u;n'}(\omega) \rho_{\nu u;n' - n'} - \Gamma_{\nu v, \nu u;n'}(\omega) \rho_{\nu u;n' - n'} - \tilde{\Gamma}_{\nu v, \nu u;n'}(\omega) \rho_{\nu u;n' - n'} \right]. \quad (22)
\]

The structure of Eq. (22) reflects the fact that the dynamics of the density matrix depends on the exchange of $n$ Floquet quanta of energy $\hbar \omega$ introduced by the hybridization with the driven reservoirs.

The explicit calculation of the Fourier-Floquet components of the rates for the model of Sec II A leads to

$$ \Gamma_{\nu v, \nu u;n'}(\omega) = \sum_{\alpha} \left[ \rho_{\nu v, \nu u,n';\alpha}(\omega) - \tilde{\Gamma}_{\nu v, \nu u;n';\alpha}(\omega) \right], $$

$$ \Gamma_{\nu v, \nu u;n'}(\omega) = \sum_{\alpha} \left[ \rho_{\nu v, \nu u,n';\alpha}(\omega) - \tilde{\Gamma}_{\nu v, \nu u;n';\alpha}(\omega) \right] \quad (23) $$

with
\[
\Gamma_{vl,ju,\alpha,n'}^0(\omega) = \sum_{\alpha,\sigma} \frac{\lambda_{vl\sigma}^* \lambda_{ju\sigma}}{2} \gamma_{\alpha\sigma} f_{\alpha}(\Delta_{uj} - n\hbar \omega) \left[ \delta_{n,n'} + \frac{A_\alpha}{2} (\delta_{n,n'+1} + \delta_{n,n'-1}) \right] \left[ \delta_{n,0} + \frac{A_\alpha}{2} (\delta_{n,1} + \delta_{n,-1}) \right]
\]
\[
\Gamma_{vl,ju,\alpha,n'}^1(\omega) = \sum_{\alpha,\sigma} \frac{\lambda_{vl\sigma}^* \lambda_{ju\sigma}}{2} \gamma_{\alpha\sigma} (f_{\alpha}(\Delta_{uj} - n\hbar \omega) - 1) \left[ \delta_{n,n'} + \frac{A_\alpha}{2} (\delta_{n,n'+1} + \delta_{n,n'-1}) \right] \left[ \delta_{n,0} + \frac{A_\alpha}{2} (\delta_{n,1} + \delta_{n,-1}) \right]
\]
and
\[
\Gamma_{ju,ul,\alpha,n'}^0(\omega) = -\sum_{\alpha,\sigma} \frac{\lambda_{ju\sigma}^* \lambda_{ul\sigma}}{2} \gamma_{\alpha\sigma} (f_{\alpha}(\Delta_{ul} - n\hbar \omega) - 1) \left[ \delta_{n,n'} + \frac{A_\alpha}{2} (\delta_{n,n'+1} + \delta_{n,n'-1}) \right] \left[ \delta_{n,0} + \frac{A_\alpha}{2} (\delta_{n,1} + \delta_{n,-1}) \right]
\]
\[
\Gamma_{ju,ul,\alpha,n'}^1(\omega) = -\sum_{\alpha,\sigma} \frac{\lambda_{ju\sigma}^* \lambda_{ul\sigma}}{2} \gamma_{\alpha\sigma} (f_{\alpha}(\Delta_{ul} - n\hbar \omega) - 1) \left[ \delta_{n,n'} + \frac{A_\alpha}{2} (\delta_{n,n'+1} + \delta_{n,n'-1}) \right] \left[ \delta_{n,0} + \frac{A_\alpha}{2} (\delta_{n,1} + \delta_{n,-1}) \right].
\]

We notice that the differences between Floquet indices ±1 entering in the above equations is a consequence of the fact that the driving depends on a single harmonic. In the above expressions we have denoted \( \Delta_{uv} = E_u - E_v \). Importantly, all the information on the temperature \( T \) and chemical potential \( \mu_\alpha \) of a given reservoir is encoded in the Fermi distribution functions, \( f_{\alpha}(\epsilon) = 1/(e^{(\epsilon - \mu_\alpha)/k_B T} + 1) \). The chemical potential only contains the corresponding DC component of the bias. This approximation is valid when \( V_{AC} \ll V_{DC} \), otherwise Eqs. (24) and (25) include further Bessel functions to take into account the time-dependence of the electrode’s Green’s function \[18\] \[19\]. For convenience, we define the hybridization function for and electron with spin \( \sigma \),
\[
\gamma_{\alpha\sigma} = 2\pi \rho_{\alpha\sigma} |w_{\alpha}|^2 = \frac{1}{2} (1 + 2\sigma P_\alpha) \gamma'_{\alpha}
\]
which depends on the spin-dependent density of states \( \rho_{\alpha\sigma} \). Here we have also defined the polarization \( P_\alpha \) and \( \gamma'_{\alpha} = 2\pi \rho_{\alpha} |w_{\alpha}|^2 \).

Finally, we also add the normalization condition. Since \( \sum_\alpha \rho_{\alpha} = 1 \Rightarrow \sum_\alpha e^{i\omega t} \rho_{\alpha} = 1 \). If we multiply by \( e^{i\omega t} \) and integrate over \( t \), we obtain \( \sum_\alpha \rho_{\alpha} = \delta_{n,0} \).

C. Current through the impurity

One interesting observable is the current that goes through the impurity as a response to the bias voltage. We can proceed along similar lines as in the derivation of the master equation for the density matrix. The current flowing out of the lead \( \alpha \) is defined as \( I_\alpha = -e \frac{d(N_\alpha)}{dt} \), which explicitly reads
\[
I_\alpha(t) = \frac{e}{\hbar} \sum_{kj} \left( w_{\alpha} \lambda_{kj\alpha} G_{ij,\alpha,\sigma}(t, t) \right) - w_{\alpha}^* \lambda_{kj\alpha}^* G_{ij,\alpha,\sigma}^<(t, t, t).
\]

Following the same procedure as before
\[
I_\alpha(t, \omega) = \frac{2e}{\hbar} \sum_{ij} \sum_{nn'} e^{-i\omega t} \text{Re} \left[ \rho_{\alpha, n-n'} \Gamma_{ij,ju,\alpha,n'}(\omega) \right].
\]

In the derivation of the previous expression we have used the fact that \( \Gamma_{ij,ju,\alpha}(t) = -\Gamma_{ju,ij,\alpha}(t) \) and defined
\[
\Gamma_{vl,ju,\alpha,n'}(\omega) = \Gamma_{vl,ju,\alpha,n'}^0(\omega) + \Gamma_{vl,ju,\alpha,n'}^1(\omega).
\]

Therefore, by computing the rates and the Floquet density matrix elements we can calculate the current. For the specific time dependent hopping \( w_\alpha(t) \) defined in Eq. [6], \( n' \) can take the values \(-2, -1, 0, 1, 2\). We notice that only these Floquet indices contribute as a consequence of the single-harmonic driving. From here on, we are going to consider the driving to be small so that we can neglect the \( A_\alpha^2 \) terms in the rates.

D. DC regime: Lifetime and decoherence time

We now focus on the steady state limit, which corresponds to \( A_\alpha = 0 \). Therefore, the stationary rates introduced in Eq. [19] reduce to \( \Gamma_{vl,ju}(t) = \Gamma_{vl,ju,0} \) and \( \Gamma_{ju,ul}(t) = \Gamma_{ju,ul,0} \). In this case, we can proceed as in the treatment of the Bloch-Redfield equation to define the lifetime of a given state as well as the dephasing time [50]. We summarize below the main steps.

In order to define the lifetime we focus on Eq. [18] for the diagonal elements of the density matrix – populations – assuming that the non-diagonal ones – coherences – do not contribute. By using the property \( \Gamma_{ij,iv,0} = -\Gamma_{ji,ui,0} \), the corresponding equation reads
\[
\dot{\rho}_{ii}(t) = 2 \sum_{v \neq i} \left[ \Gamma_{vl,iv;0} \rho_{iv}(t) - \Gamma_{vl,vi;0} \rho_{vi}(t) \right],
\]
where we identify the inverse of the population life time of the state \( |i\rangle \) by
\[
\frac{1}{T_i} = \frac{2}{\hbar} \sum_{v \neq i} \Gamma_{vl,vi;0}.
\]

Notice that if the state \( |i\rangle \) corresponds to a many-body state with single-electron occupancy, \( v \) runs over all the states with zero-electron occupancy.

Similarly, if we now focus on the coherences of Eq. [18]
we get

\[ \hbar \rho_{lj}(t) - i \Delta_{lj} \rho_{lj}(t) = - \sum_v (\Gamma_{lv,vlj} + \Gamma_{lj,vlj}) \rho_{lj}(t) + \ldots \]  

(32)

where \( l \neq j \) and correspond to singly-occupied states while \( \ldots \) denotes the other terms of the master equation. The sum over \( v \) runs over empty states. As the rates entering this equation correspond to second-order tunneling processes between the impurity and the reservoirs, coherences with \( l \) corresponding to an empty state and \( j \) corresponding to a singly-occupied one or vice-versa are zero. Eq. (32) leads to the following definition of the inverse of the coherence time

\[ \frac{1}{T_{2j}^l} = \frac{1}{\hbar} \sum_v (\Gamma_{lv,vlj} + \Gamma_{lj,vlj}). \]  

(33)

Hence we can identify a relation between the coherence time and the relaxation times

\[ \frac{1}{T_{2j}^l} = \frac{1}{2} \left( \frac{1}{T_1^l} + \frac{1}{T_1'} \right). \]  

(34)

We notice the lack of pure dephasing time in this description. This is because, for the type of bath we are considering, the fluctuation between two singly occupied states of the impurity necessarily implies a second-order charge fluctuation. Hence, the rates of the form \( \Gamma_{ll,jj} \) are zero.

### E. AC regime: Rabi frequency

The Rabi frequency of a magnetic system under a static magnetic field and driven by time-dependent transverse magnetic field is defined as the transfer rate of the population of one state towards the other state induced by the periodic driving. The latter is represented by a time-oscillating term in the off-diagonal matrix elements of the Hamiltonian expressed in the basis of the spinors in the direction of the static magnetic field.

Contrary to the standard ESR [4], here we are not considering a time-dependent periodically driven magnetic field. In fact, the only time-dependent term of our model is in the form of the periodically modulated hybridization of the impurity level and the leads, see Eq. (10). We analyze now the possibility of inducing an oscillating transfer rate of the populations of the different states of the impurity, akin to the Rabi oscillations, as a consequence of the electrical AC bias.

We focus on \(|l\rangle\) being a singly-occupied state of the impurity. The evolution of the corresponding population is given by

\[ \hbar \dot{\rho}_{ll}(t) = 2 \sum_v \{ \text{Re}[\Gamma_{vl,lv}(t)\rho_{lv}(t) - \text{Re}[\Gamma_{lv,vl}(t)\rho_{vl}(t)] + \sum_{vu,v \neq u} \left[ \Gamma_{vl,lu}(t)\rho_{uv}(t) - \bar{\Gamma}_{lv,ul}(t)\rho_{uv}(t) \right] - \sum_{vu,v \neq u} \left[ \Gamma_{lv,vu}(t)\rho_{vu}(t) - \bar{\Gamma}_{vl,uv}(t)\rho_{vu}(t) \right] \}, \]  

(35)

where, as already mentioned \( v \) runs over empty states for \( l \) labeling a singly-occupied one.

We extend the previous definition of Eq. (31) of the inverse of the life time to the present case, where we are considering time-dependent rates, as follows

\[ \frac{1}{T_{1t}^l}(t) = \frac{2}{\hbar} \sum_{v;1 \neq l} \text{Re}[\Gamma_{vl,lv}(t)], \quad \frac{1}{T_{1l}^t}(t) = \frac{2}{\hbar} \text{Re}[\Gamma_{vl,lv}(t)]. \]  

(36)

We have also introduced the inverse of the life time \( T_{1l}^t(t) \). We identify the terms connecting coherences as Rabi-type terms,

\[ \frac{\hbar \Omega_{lu}^l(t)}{2} = \Gamma_{vl,lu}(t) = -\bar{\Gamma}_{lv,ul}(t). \]  

(37)

Introducing this definition, Eq. (35) reads

\[ \dot{\rho}_{ll}(t) = \sum_v \frac{\rho_{vu}(t)}{T_{1l}^v(t)} - \frac{\rho_{ll}(t)}{T_{1l}^l(t)} + \sum_{vu,v \neq u} \text{Re}[\Gamma_{vl,lu}(t)\rho_{vu}(t)] - \sum_{vu,v \neq u} \text{Re}[\Gamma_{lv,ul}(t)\rho_{vu}(t)]. \]  

(38)

The transition amplitudes can be Floquet-Fourier transformed. The Floquet sum can only take values from \(-2\) to \( 2 \), see Eq. (24). For \( \omega \) much smaller than the inverse of any other characteristic time of the problem, we can perform the approximation that the Fermi distribution in the rates functions, Eqs. (24) and (25), do not depend on \( \omega \) strongly. Under this assumption, plus neglecting terms proportional to \( A_2^2 \) and considering no coherence at zero driving, Eq. (39) can be further simplified and reads

\[ \dot{\rho}_{ll}(t) = \sum_v \frac{\rho_{vu}(t)}{T_{1l}^v(t)} - \frac{\rho_{ll}(t)}{T_{1l}^l(t)} + \sum_{vu,v \neq u} \left[ \Omega_{vl,lu}^v(t)\rho_{vu}(t) + \rho_{vl}(t) \right] \cos \omega t - \sum_{vu,v \neq u} \left[ \Omega_{lv,ul}^v(t)\rho_{vu}(t) + \rho_{ul}(t) \right] \cos \omega t, \]  

(39)

which resembles the Bloch-Redfield master equation with the Rabi term. Therefore, we identify from this equation the Rabi frequency of our model

\[ \hbar \Omega_{lu;1} = \hbar \sum_v \Omega_{vl,lu}^v = \hbar \sum_v \Omega_{lv,lu;1} + \hbar \sum_v \Omega_{lv,ul;1} = 2 \sum_{\alpha} A_{\alpha} \left( \Gamma_{lv,vu,\alpha;0}^0 - \Gamma_{lv,vu,\alpha;0}^1 \right), \]  

(40)
FIG. 2. Static energy scheme of the $S_T = 1/2$ QI Hamiltonian (right) and the cotunneling configurations (left). Plots a) and b) are one-electron energy schemes representing a QI system at zero and finite bias, while panels c) and d) show the many-body energies of the corresponding states involved in the tunneling process. The chemical potential for both electrodes is taken as the reference level, $\mu_{L,R} = 0$. At zero-bias, a) and c), no net current is passing through the QI. In the QI configurations zero magnetic field $|1\rangle \equiv |\downarrow\rangle$ and $|2\rangle \equiv |\uparrow\rangle$. State $|3\rangle$ is the empty state of the QI. Here $\varepsilon_{\alpha} < 0$ such that the up and down states are energetically below the empty one. In order to induce a current through the QI and arrive to pictures b) and d), we apply a DC bias voltage such that $eV_{DC} = \mu_L - \mu_R > 0$, by decreasing $\mu_R$ while, symmetrically, increasing $\mu_L$ until the absolute value of the right Fermi energy level is larger than the difference $\Delta_{31} = -\varepsilon_1 - g\mu_B |B|/2$. Similarly, $\Delta_{32} = -\varepsilon_2 = -\varepsilon_1 + g\mu_B |B|/2$.

This quantity is found to be zero for non-polarized reservoirs ($P_\alpha = 0$).

Eq. (39) can be cumbersome to solve analytically. However, numerical calculations suggest that the populations contribute with a term proportional to the square of Rabi frequencies, while the coherences have a linear dependence on this quantity. This is also what other studies found employing the rotating wave approximation [27, 30]. Therefore, the DC current, $n = 0$ in Eq. (28), behaves as $I_{n=0}^{DC}(\omega) \propto \sum_{\Omega \in \{1,0\}} \Omega_{\Omega \in |\mu|}$ at the corresponding resonance frequencies between filled states $|\downarrow\rangle$ and $|\uparrow\rangle$.

III. RESULTS FOR $S_T = 1/2$

The simplest case corresponds to an impurity with $S = 0$ for the localized spin degrees of freedom. Hence, the total spin when the external orbital is singly occupied is $S_T = 1/2$. This configuration is equivalent to a quantum dot with large charging energy ($U \rightarrow +\infty$), which has only three many-body states, corresponding to two occupied levels (spin up and down) and an empty level, as shown in the scheme of Fig. 2.

To illustrate the workings of our ESR mechanism, we fix the model parameters so that the system is in the sequential tunneling regime. This makes the analysis particularly simple. In addition, we can expect the main features of the resonant ESR signal to remain when the current is dominated by off-resonance transport (cotunneling regime) [29]. The parameters used for the calculations of this section are as follows unless otherwise specified:

1. The magnetic field is fixed to $B = (5.0, 0, 0.2)T$, where the tip’s spin polarization fixes the $z$ axis.
2. We particularize to a weak driving regime, as expected for instance in the all-electrical STM-ESR implementations [38]. Thus, we take $A_\alpha \in [10^{-3}, 0.5]$.
3. The driving constants are $A_L = A_R = 0.05$ and the hybridization functions, $\gamma_\alpha = 2\pi \rho_\alpha |w\alpha|^2$, $\gamma_\alpha' = \gamma'_R = 50 \mu eV$.
4. The right electrode is spin polarized with $P_R = 0.35$ (see Eq. (26)).
5. The electronic level is set to $\epsilon_L = \epsilon_1 = -1 \text{ meV}$, fixing the energy difference between electronic states to $\Delta_{31} = 1.29 \text{ meV}$ and $\Delta_{32} = 0.71 \text{ meV}$, see Fig. 2.
6. The temperature is fixed at one Kelvin.

A. Static case, $\omega = 0$

We analyze now the simplest situation where the AC bias voltage is not applied, $A_\alpha = 0$. We start by considering both electrodes at zero chemical potential $\mu_0 = 0$, as indicated in Fig. (a) and c). Next, we change symmetrically the chemical potentials of the electrodes with respect to this value, $\mu_L = -\mu_R = eV_{DC}/2$. The resulting populations are plotted as a function of the applied bias in Fig. (b). At low bias, the ground state $|1\rangle$ is completely populated. When the bias potential matches $2\Delta_{31}$, the chemical potential of the dot becomes resonant with the chemical potential of the right electrode, allowing tunneling of the down electron to the right electrode. Moreover, since $\Delta_{32} \leq \Delta_{31}$, the transport channel through state $|2\rangle$ will also be open. As a consequence, the three states of the QI become equally populated ($\rho_{jj} \approx 3/3$). The response to the voltage bias is also revealed in the behavior of the current, see Fig. (c). As the bias overcomes the value of $eV_{DC} = 2\Delta_{31}$, the current increases reflecting the opening of a transport channel, while it saturates at a higher bias when all channels are fully open. Correspondingly, the $dI/dV$ peaks at the current step bias $eV_{DC} = 2\Delta_{31}$.

B. AC-driven case, $\omega \neq 0$

We obtain clear ESR peaks in the long-time averaged current together with a characteristic dynamical behavior of the reduced-density matrix that allows us to unambiguously conclude that Rabi oscillations are being excited.
The long-time averaged current corresponds to the Floquet component $n = 0$ of the time-dependent current. We find it useful to analyze the following magnitude \[30\],

$$
\Delta I_{DC}(f) = I_{Off}^{DC} - I_{On}^{DC}(f),
$$

(41)

where $I_{Off}^{DC}$ is the current far from resonance satisfying two conditions: $\omega = 2\pi f$ is much larger or smaller than the Larmor frequency, and $f$ is much smaller than the $eV_{DC}/h$. The change in the population follows the same definition.

Figure 4 shows $\Delta I_{DC}(f)$ for the frequency $f$ going from zero to 1500 GHz ($\sim 6.2$ meV) when the applied bias is 7.7 mV. Below 500 GHz one narrow peak dominates the spectra. Figure 4b) shows a zoom of the low-frequency peak. This is clearly an ESR peak due to the Rabi oscillations between states $|1\rangle$ and $|2\rangle$. The origin of the oscillation is a spin-flip transition that reflects the Zeeman splitting induced by the applied magnetic field, $B$. The Larmor frequency due to the Zeeman splitting is then $g\mu_B|B|/h \approx 5.79 \times 10^{-1}/h$ meV $\approx 140$ GHz. These high-frequency steps show a strong dependence on the temperature. The shape of the steps is directly related to the Fermi occupation factors. At larger frequencies all transport channels are open and the current saturates.

The hallmark of ESR transitions is revealed in the reduced-density matrix dynamical behavior. Figure 5a shows the populations of the states as the driving frequency is ramped up. Figure 5b) shows the real and imaginary part of the coherences between states $|1\rangle$ and $|2\rangle$, that are the ones involved in the Rabi oscillation. The resonant feature is centered around the Larmor frequency. If, in Eq. (6), $C_{\alpha} \ll 1$ the change of population and coherence can be greatly increased, making the effect of the driving more efficient. The behavior of the reduced-density matrix unequivocally proves that the peak in the long-time averaged current at 140 GHz

\[ f_2 = (\Delta_{23} - E_{F_L})/h = 759 \text{ GHz}, f_3 = (\Delta_{32} + E_{F_L})/h = 1103 \text{ GHz} \] and $f_4 = (\Delta_{31} + E_{F_L})/h = 1243 \text{ GHz}$. These high-frequency steps show a strong dependence on the temperature. The shape of the steps is directly related to the Fermi occupation factors. At larger frequencies all transport channels are open and the current saturates.

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FIG. 5. Change in the populations a) and coherence, Floquet number 1, b) of the states vs frequency. The applied bias is \( V_{DC} = 7.7 \text{ mV} \). The resonance peak is found at 140 GHz. The change in the populations, \( \Delta \rho_{ll}(f) = \rho_{Off}^{ll} - \rho_{On}^{ll}(f) \), of the occupied states decrease at the resonance while the state \( |3⟩ \) increases twice in comparison. Real part of the coherence, \( n = 1 \), presents the same behaviour as the populations of the occupied states while the imaginary part has a fano shape. The changes in coherences and in populations are in the range of 0.6\% and 0.02\% respectively, which matches the relative change in current produced at the Larmor frequency in Fig. 4.

is associated to an ESR. In other words, we have demonstrated that the modulation of the tunnel barrier by an oscillating electric field is able to induce ESR.

The resonance peak in Fig. 4b) can be fitted to a Fano line shape:

\[
\Delta I_{DC} = \frac{2c}{\Gamma} \frac{1}{q^* + 1} \left[ 1 + q^*(f - f_0)/\Gamma \right] \left[ 1 + 4 \left( f - f_0 \right)/\Gamma \right]^2,
\]

(42)

where \( \Gamma \) is the width of the resonance, \( f_0 \) is the resonance frequency, \( c \) is a parameter proportional to the Rabi frequency and related to \( T_1 \) processes and \( q^* = 1/q \), being \( q \) the commonly called Fano parameter. This lineshape corresponds to a generalization of the Lorentzian profile expected from the Block equations [30]. The rate functions are contained in the width and \( c \) parameter, as well as in the Fano parameter, such that they control the line shape. For the present case, \( q^* = -0.088, c = 5.021 \text{ pA GHz} \) and \( \Gamma = 12.1 \text{ GHz} \), therefore \( I_{peak} \approx 2c/\Gamma = 0.82 \text{ pA} \).

FIG. 6. a) Change in the current vs frequency close to the resonance for a magnetic field \( \mathbf{B} = (5, 0, 0.2)T \). The resonance peak height grows quadratically with the polarization. This is demonstrated in panel b) where the peak height (main panel) and the Rabi frequency (inset) are plotted as a function of \( P_R^2 \) and \( P_R \) respectively.

pA. In more general cases where the peak is affected by other factors such as high-frequency transitions, thermal broadening or asymmetric conditions, more complex shapes of the ESR spectra may occur.

1. Spin polarization of the electrodes

Let us study the role of the electrode polarization evaluating the previous ESR resonance for four different right-electrode spin polarizations: \( P_R = 0, 0.35, 0.7, 1 \). Negative values of the polarization –implying the right-electrode magnetic moment is antiparallel to the \( z \)-component of the magnetic field– it just introduces a \( \pi \)-phase change in the coherences at resonance. The coherences change is due to the sign change in the Rabi frequency, Eq. (40), and does not affect the long-time averaged current or the population since they depend on the square of the Rabi frequency. Fig. 6a) shows the resonance for different polarizations. As expected, zero polarization leads to zero coherence since we have a zero Rabi frequency (because \( \Gamma_{1332:1} = 0 \)), therefore, no resonance peak emerges. The maximum Rabi frequency is achieved for a half-metal (\( |P_R| = 1 \)). In fact, one can no-
tice that the resonance peak height scales as \( I_{\text{peak}} \propto P_R^2 \). Interestingly, this matches the experimental observations of Ref. 10 where \( I_{\text{peak}} \) is found to be proportional to the square of the Rabi frequency, \( \Omega^2 \), under the constrain that \( \Omega T_1 T_2 \ll 1 \), with \( T_1 \) and \( T_2 \) the involved life and coherence times, respectively.

From Eq. (40), the calculated Rabi frequency is

\[
h \Omega_{12;1} = A_R \lambda_{31}^* \lambda_{32} \gamma_R P_R / 2,
\]

where we used \( \lambda_{31}^* \lambda_{32} = -\lambda_{1}^* \lambda_{2} \). Since the change in the current is proportional to \( P_R^2 \) and only the Rabi frequency depends strongly on the polarization, we conclude that \( I_{\text{peak}} \propto \Omega^2_{12;1} \). This is clearly observed in Fig. (b) where the peak height follows a perfect linear dependence on the square of the polarization.

Equation (43) makes clear the key role of the electrode polarization. First, because without polarization there is not peak since we have no Rabi term. Second, because it gives an axis of quantization of the spin that is going to determine the role of the external magnetic field and the substrate anisotropy. Indeed, these three axes need to be considered in order to understand the degree of spin mixing and existence of resonances in any possible system [31].

The role of the electrode spin polarization can be qualitatively understood by its effect on selecting certain transport spin directions and forcing spin-flip components to the time-dependent current. In the absence of spin polarization, the higher-order spin-flip transitions will become negligible in comparison to the lower-order transition that is the direct transfer of an electron from electrode \( L \) into \( R \) through either state \( |1\rangle \) or state \( |2\rangle \) without spin-flip. In the presence of spin polarization, say 100% spin-up polarized \( R \) electrode, any spin down electron from the \( L \) electrode need to spin-flip to reach the \( R \) electrode and contribute to the current.

Interestingly, the width \( \Gamma \) of the ESR resonance remains constant as the polarization changes. In fact, the width is proportional to the inverse of the coherence time \( 1/T^2 \), which also remains essentially constant as the polarization changes. The same behavior is obtained in the framework of Bloch-Redfield theory [12, 30].

2. Driving amplitude

The driving term is obviously essential to have any resonance signal. We found that the driving is proportional to the applied alternating bias, \( V_{AC} \). It is then instructive to study how the ESR amplitude depends on the applied bias. Using the parameters in Sec. IV B leads to Fig. 7. Clearly, zero driving implies no resonance while increasing the driving provides a higher peak. One can notice in the inset of Fig. 7 that the Rabi is clearly linear with the driving amplitude that implies a quadratic dependence on the current peak. This is not a surprise recalling the behavior of the DC component of Eq. (28). The exact dependence on the driving is hidden in the Floquet density matrix elements that are connected to four Floquet numbers \( \pm2 \) as we mentioned in Sec. II. Moreover, we found that \( I_{\text{peak}} \propto \sum_{\pm2 \neq \pm1} [\Omega_{12;1}]^2 \).

For large \( V_{AC} \), the Taylor expansion leading to Eq. (6) will break down and higher harmonics of \( \omega \) will contribute, leading to the experimentally found saturation of the ESR peak with applied bias [10].

3. Dependence with temperature

The main temperature effect on the ESR at large DC voltage is to enhance the decoherence rate, \( h/\Omega^2 \), that leads to wider and smaller ESR peaks. However, increasing the temperature leads to additional changes in the \( \Delta I_{DC} \) resonance profile. This is shown in Fig. 8a). Interestingly, the reduction of the ESR height is not only due to the increase of the resonance width. Indeed, we find a reduction of the Rabi frequency as the temperature increases, Fig. 8b). The temperature dependence of the Rabi frequency implies an intrinsic reduction of the efficiency of the spin-flip process to produce the ESR.

Between 0.1 K and 1 K we are in the condition that all electronic channels are open, \( |eV_{DC}| \gg k_B T \), \( \Delta_{21} \), the non-adiabatic decoherence (also known as population scattering) is controlled by the bias voltage, and not by the thermal broadening [30]. As seen in Fig. 8a) and b), there is not evolution in the small temperature range.

As the temperature increases, the ESR peak amplitude decreases, being barely observable for \( k_B T \gg |eV_{DC}| \), \( \Delta_{21} \). However, the Rabi frequency tends to saturation, Fig. 8b), showing that ESR is active despite being barely observable.

Another source of temperature dependence that we have not considered here is the variation of the tip-polarization with the temperature [11, 13]. This could be easily implemented to compare with the experimental
FIG. 8. Current change a) and Rabi frequency b) for different temperatures. The resonance peaks for the 0.1 and 1 K coincide, reflecting the fact that at the present parameters low-temperature decoherence is produced by the applied bias. As the temperature increases, the ESR becomes wider and shorter as a consequence of the enhanced decoherence. Surprisingly, the Rabi frequency also decreases with temperature, showing that temperature also has an influence on the coupling between resonating states beyond the effects of decoherence. The ESR peak height scales with the square of the Rabi frequency, such that an additional reduction in the Rabi frequency translates into a considerable reduction of the resonance peak.

results at various temperatures.

4. Magnetic-field dependence

In the case of spin-1/2 systems, the perpendicular magnetic field \( B_x \) is essential to have any sort of coherence since it allows having states \(|1\rangle\) and \(|2\rangle\) with mixed character, which is necessary to have an ESR-active system \[38\]. In order to illustrate the role of \( B_x \), we fix all the parameters except \( B_x \) to those introduced in Sec. 3B Figure 3) shows the results of \( \Delta I_{DC} \) as a function of the driving frequency \( f \) for different values of \( B_x \). At zero transverse field, no resonance peak appears. As \( B_x \) increases, a resonance peak develops in the frequency position determined by the total magnetic field. The peak height is related to the strength of the state

FIG. 9. a) Change in the long-time averaged current vs driving frequency for different values of the \( x \)-component of the magnetic field, \( B_x \), while keeping the \( z \)-component fixed at 0.2 T. The spectra shift linearly with \( B_x \) following the Zeeman shift. Zero \( B_x \) field leads to no resonance, and increasing it provides a needed mixture of states \(|1\rangle\) and \(|2\rangle\) that rapidly saturates. The resonance peak positions from lower to higher are: 15.07, 140.06, 559.84 GHz. In b) the resonance peak height is plotted as a function of \( B_x \). The saturation of state mixing is reached at 2 T and as a consequence, the peak height also saturates. The fitting curve is \( aB_x^2/(B_x^2 + b) \) where \( a = 0.82 \) pA, \( b = 0.053 \) T\(^2 \sim B_x^2 \) showing that it is proportional to the square of the Rabi frequency, Eq. \( (44) \). Panel c) shows the inverse of the Fano parameter, \( q^* \) (inset), and the resonance FWHM as a function of \( B_x \). These data show that the line profile becomes closer to a Lorentzian profile as the magnetic field increases because the Larmor frequency fixed by the Zeeman energy increases, placing the resonance away from zero frequency.
mixing $[7,38]$. We have shown in the polarization section $[33]$, that for the three-level case of $S_T = 1/2$, the Rabi frequency is proportional to $\lambda_{31_T}^{32}\alpha$. The eigenvectors of the impurity Hamiltonian are:

$$
|1\rangle = \frac{1}{\sqrt{2B}} \frac{1}{\sqrt{B + B_z}} [B_z | \downarrow \rangle + (B - B_z) | \uparrow \rangle],
$$

$$
|2\rangle = \frac{1}{\sqrt{2B}} \frac{1}{\sqrt{B - B_z}} [(B_z - B) | \downarrow \rangle - B_z | \uparrow \rangle],
$$

$$
|3\rangle = [0].
$$

Hence, (3) corresponds to an empty electronic level. Here, $B = \sqrt{B_x^2 + B_z^2}$. These results show that only if $B_x \neq 0$, $|1\rangle$ and $|2\rangle$ contain both spin up and down components, enabling Rabi oscillations $[32]$.

Using these eigenstates, we can calculate the projections entering the Rabi frequency expression. We get

$$
\hbar \Omega_{12;1} = A_R \sum_{\sigma} \lambda_{31_T}^{32}\alpha(1/2 + \sigma P_R)\gamma_R
$$

$$
= A_R P_R \gamma_R B_x/2B \propto \sqrt{B_x^2 - B_z^2} (44)
$$

that tends to a constant value as $B_x$ increases. This is shown in Fig. 9b). Notice that in this case, for values $B_x > 2$ T saturation is attained, reflecting that the mixing of spin up and down states cannot be further enhanced by the $x$-component of the magnetic field for a fixed valued of $B_z = 0.2$ T.

Furthermore, the magnetic field can affect the Fano parameter and the width of the resonance. The inset of Fig. 9c) shows the $q^\alpha$ dependence on the $x$-component of the magnetic field. Only at very low magnetic fields $|q^\alpha|$ increases drastically. This is due to the distorted resonance profile close to zero frequency, which is also reflected in the values of the full width at half maximum (FWHM), Fig. 9c). As the values of $B_x$ increase, the ESR moves away from zero frequency and develops a full-fledged Fano profile. The FWHM becomes constant then, since it is proportional to the inverse of the coherence time, $1/T_2^2$.

**IV. RESULTS FOR TWO COUPLED SPINS $S_T = 0, 1$**

In this section we illustrate the workings of the tunneling-induced ESR for two interacting spin-1/2 systems, where one of them is coupled to two electrodes. Thus, we consider a localized $S = 1/2$ spin exchange coupled to the electronic level that transfers electrons between the two biased electrodes. Hence, the electronic level acts as an extra spin-1/2 system when it is singly occupied. The basis set of the impurity is given by the tensor product of the three states of the electronic level (down, up and empty) times the two states of the coupled spin-1/2 (down and up), a total of six states.

Figure 10 shows a sketch of the system. In the coupled case, assuming a ferromagnetic coupling ($J < 0$) and $|J|$ larger than the Zeeman splitting the full system becomes a $S_T = 1$ spin. The triplet states are energetically below the singlet state, leading to an effective spin-1 situation. Contrary, if the coupling is anti-ferromagnetic ($J > 0$), the singlet state is the one with the lowest energy and the spin of the system is $S_T = 0$. When $J$ is close to zero, we have a decoupled $S_T = 1/2$ spin and the corresponding results can be found in the previous section.

Hence, this model allows us to explore the physics of ESR in a magnetic impurity of spin $S_T = 1$, or of two impurities of spin 1/2. In particular, this last case has been carefully analyzed in a series of STM-ESR experiments on two Ti atoms, at different distances on a MgO/Au (100) substrate $[11,13]$. The distance between the two Ti atoms control the exchange coupling strength $J$, and the bias between tip and sample contains an alternating component. The measured DC tunneling current shows four distinct peaks at different driving frequencies that have been associated with singlet-triplet transitions under an external magnetic field and the local field of the magnetic tip $[11,13]$.

If $J$ and the transverse magnetic field are non zero, the filled and empty states are mixed, making possible the appearance of resonances between states with $\Delta S_{T,z} = S_{T,z} - S_{T,z} = \pm 1$ (spin flip), where $i$ and $j$ can be any state, labeled by 1 to 6 in Fig. 10. For the sake of simplicity, we set $D = 0$ eV in Eq. (3).

Similar to the $S_T = 1/2$ case analyzed in the previous section, the current is computed on the left electrode in a situation of large DC bias voltage where all the states are properly connected through the sequential tunneling. The other parameters are: i) Driving amplitude $A_\alpha = 0.5$, ii) polarization $P_R = 0.45$, iii) Temperature $T = 1K$. The parameters describing the hybridization with the reservoirs are iv) Coupling constants $\gamma_R = 0.5$ $\mu$eV and $\gamma_L = 5$ eV that allow us to reproduce an overall long-time averaged current of 50 pA. Truncating the Floquet components at $n = 5$ is enough to get a converged solution of the time-dependent master equation.
In order to take into account the local magnetic field of the tip, we add a new Zeeman term to the impurity Hamiltonian that only affects localized electrons. The origin of this field in the experimental setup is the magnetic interaction exerted by the tip on the atom underneath. We label this field as $B_{\text{tip}}$ following the notation of Ref. [13].

Figure 11 shows the result of our calculation. Due to the presence of two different magnetic fields, we find four resonance peaks. The values are: 0.051, 0.087, 0.12, 0.13 GHz respectively. The order of the resonance peaks is, from low to high frequencies: transition singlet to the triplet state $S_{1}^{-}$, transitions between the triplet states $S_{T,z} = 0$ and $S_{T,z} = \pm 1$ and finally singlet to triplet state $S_{T,z} = 1$ transition, in good agreement with the experimental interpretation [13].

The frequency spectra can be fitted to Fano lineshapes as in the previous section. This allows us to characterize each resonance peak identifying the asymmetry through the Fano parameter, plus the peak height and width. These parameters can be associated to the Rabi frequency, the coherence and life times of each transition. The Rabi frequency controls the peak height and the coherence time, $T_{2}$, the width, similar to the $S_{T} = 1/2$ case. Every Rabi frequency is proportional to the polarization, but now the strength of the peak does not depend on it linearly. As we increase the (positive) polarization, the right electrode accepts more spin-up than spin-down electrons. Therefore, only the transitions from the triplet state with $S_{z} = -1$ to any of the two $S_{z} = 0$ states are possible, since they involve flipping the spin of the incoming electron from down to up. The frequency spectra will then have two peaks: the first and the third transitions in Fig. [11].

From the fitting analysis, we notice an increase of the width of the peaks as the driving frequency increases. This happens because we are in an asymmetric coupling case where $\gamma_{L}' \gg \gamma_{R}'$. It also generates more asymmetric Fano lineshapes. The first and third resonances have negative and similar inverse Fano factors, $q^{*}$, equal to -0.07 and -0.03 respectively, while the other two transitions have positive values equal to 0.2 and 0.007 for the second and fourth transition.

V. SUMMARY AND CONCLUSIONS

We have presented a theory based on non-equilibrium Green’s functions and Floquet theory to compute the driving of the magnetic degrees of freedom induced by a time-dependent voltage drop between two reservoirs. The spins are coupled via a Kondo-like Hamiltonian with the flowing electrons, permitting us to analyze recent experimental observations where an STM is used to drive single-atom spins using alternating bias in the GHz-frequency range.

The theory uses an expansion on the electronic hopping matrix elements to lowest order to obtain the reduced density matrix. The resulting quantum master equation depends on time and can be solved using a Floquet expansion. The long-time average corresponds to taking the first Floquet term, $n = 0$, of the different evaluated quantities. In this way, we can obtain the long-time averaged electron current that is directly comparable with experimental measurements.

A magnetic atom is modeled by a single electron orbital that is coupled via a single hopping term to each electrode. The electron entering the atom interacts with the rest of the atomic spin via a magnetic exchange coupling that reduces to a Kondo-like Hamiltonian between the electron in the atomic orbital and the rest of the spin. The atom is also subjected to magnetic fields. Magnetic anisotropy terms can be introduced to reproduce the experimental conditions. Following previous studies [21, 38], we have assumed that the time-dependent electric field couples to the spin via the modulation of the tunneling barrier. This reflects into a time-dependent hopping term and, as we have shown in the results of this work, it is enough to drive local spins. The model and theory presented here are very rich and allow us to account for many of the features found in STM-ESR experiments.

We have evaluated the cases of an atom of total spin $S_{T} = 1/2$ that is contained in the spin of the electron that hops on and off the atom. We have clearly shown that under a driving external electric field, we do have Rabi oscillations and that an ESR is established. Our theory has permitted us to define the strength of the Rabi frequency, and correlate it with the height of the resonance. Moreover, we have computed the coherence time, $T_{2}$ and shown that it is related to the width of the ESR. Following the experimental studies of two Ti atoms with STM-ESR,
we have successfully replicated the main experimental ingredients, showing the information contained in the line profiles of the ESR.

Other calculations that we have not presented in this work, successfully reproduce the main experimental STM-ESR results for Fe adsorbates, showing that indeed fourth-order Stevens operators are necessary to have ESR.\[4\]

Although the basic ingredient for driving the spin is the same as in Ref.\[38\], i.e., a modulation of the hybridization with the electrodes, there is a fundamental difference between both works. Reina et al.\[38\] considered the time-dependent Lamb shift induced by the hybridization with the leads in the STM junction. However, the Lamb shift has not been considered in this work because the energy shift exactly cancels due to the symmetric bias drop and other approximations employed here. In STM-ESR conditions, the Lamb shift can be important.

It is also worth pointing out the difference with Refs.\[28\] and \[29\], where the main objective was to study the influence of the driving on the spin dynamics. However, in the present work, our target was to demonstrate the driving of a spin system induced by variations in the hybridization with electrodes.

As possible extensions of the present work, we can mention to go beyond the \(U \rightarrow \infty\) approximation, as well as to include higher-orders in the hopping to account for pure-dephasing contributions to the decay of coherences reflected in a smaller \(T_2\). Our theory allows us to treat the cotunneling regime that directly applies to STM-ESR as we will do in a forthcoming publication.

In summary, the theory presented here seems to be complete and flexible enough to explain and predict STM-ESR results, allowing us to explore the possibility of quantum control experiments with the STM.

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A. DERIVATION OF THE FLOQUET MASTER EQUATION

Our aim in this appendix is to derive Eq.\[22\] from Eq.\[15\]. To this end, first we need to compute the mix Green’s Function using Langreth theorem in the Schwinger-Keldysh contour:

\[
G_{ij,\sigma}(t,t') \approx \int dt_1 \sum_{uv} \lambda_{\sigma \sigma} w_\sigma(t_1) \times
\left[ g_{ij,uv}(t,t_1)g_{\sigma \sigma}^<(t_1-t') + g_{ij,uv}^<(t,t_1)g_{\sigma \sigma}^<(t_1-t') \right]
\]

(45)

and

\[
G_{\alpha \alpha,ij}(t,t') \approx \int dt_1 \sum_{uv} \lambda_{uv \sigma} w_\sigma(t_1) \times
\left[ g_{\alpha \alpha}^<(t-t_1)g_{uv,lj}^<(t_1,t') + g_{\alpha \alpha}^<(t-t_1)g_{uv,lj}^<(t_1,t') \right]
\]

(46)

where we have introduced the Green’s functions of the electrodes and the one of the isolated impurity. We also considered the weak coupling approximation. The isolated lesser Green’s function of the system is defined as \(g^\lesssim_{\sigma \sigma,ij}(t,t') = i(\bar{\rho}_{ij}(t')\rho_{uv}(t))\). Since the Green’s function of the reservoirs does not have a periodic structure, we can work directly on the energy space and get: \(g^\lesssim_{\sigma \sigma,ij}(t,t') = i f_\alpha(\epsilon)\text{Im}[g^\lesssim_{\alpha \sigma}(\epsilon)]\), and \(g^\lesssim_{\sigma \sigma}(t,t') = i(1-f_\alpha(\epsilon))\text{Im}[g^\lesssim_{\alpha \sigma}(\epsilon)]\), with \(\text{Im}[g^\lesssim_{\alpha \sigma}(\epsilon)] = 2\pi \sum_{k=0}^\infty |\epsilon_\alpha(k)|\delta(\epsilon-k_\alpha)\). The periodic time-dependence appears in the self-energy through the tunneling parameters and it is defined as:

\[
\Sigma^c_{\alpha \sigma}(t,t') = \sum_k w^*_\alpha(t)g^c_{\alpha \alpha}(t-t')w_\sigma(t'),
\]

(47)

whose Floquet-Fourier components are

\[
\Sigma^c_{\alpha \sigma,nn,\epsilon}(\epsilon) = \sum_k \left|w^0_\alpha\right|^2 \left[ \delta_{n,0} + \frac{A_\alpha}{2} (\delta_{n-1} + \delta_{n,1}) \right]
\times g^\lesssim_{\alpha \sigma}(\hbar\epsilon) \delta_{\epsilon,0} + \frac{A_\alpha}{2} (\delta_{\epsilon,-1} + \delta_{\epsilon,1}),
\]

(48)

with \(c = r, a, >, <\). For convenience we introduce the definitions

\[
\Lambda_{ij,\sigma}(t) = \int dt_1 \sum_{uv} \mu_{uv \sigma} \times
\left[ g^<_{ij,uv}(t,t_1)\Sigma^c_{\alpha \sigma}(t_1,t) + g^<_{ij,uv}(t,t_1)\Sigma^c_{\alpha \sigma}(t_1,t) \right]
\]

(49)

\[
\tilde{\Lambda}_{\alpha \sigma,ij}(t) = \int dt_1 \sum_{uv \sigma} \lambda_{uv \sigma} \times
\left[ \Sigma^c_{\alpha \sigma}(t,t_1)g^<_{uv,lj}(t_1,t) + \Sigma^c_{\alpha \sigma}(t,t_1)g^<_{uv,lj}(t_1,t) \right]
\]

(50)

so that we can rewrite the master equation as follows:

\[
\hat{\rho}_{ij}(t) = \frac{i}{\hbar}(E_i - E_j)\rho_{ij}(t) + \frac{1}{\hbar} \sum_{\alpha \sigma \tilde{\alpha}} \left[ \lambda_{\alpha \sigma} \tilde{\Lambda}_{ij,\alpha \sigma}(t) - \lambda_{\alpha \sigma} \tilde{\Lambda}_{\alpha \sigma,ij}(t) \right] \left[ \lambda_{\alpha \sigma} \Lambda_{ij,\alpha \sigma}(t) + \lambda^*_{\alpha \sigma} \Lambda_{\alpha \sigma,ij}(t) - \lambda_{\alpha \sigma} \Lambda_{\alpha \sigma,ij}(t) \right],
\]

(51)
Let us focus on the isolated system. Following the equation of motion for the uncoupled central system Hamiltonian $\hat{\rho}_{ij}(t) = \frac{i}{\hbar}(E_i - E_j)\hat{\rho}_{ij}(t)$, then $\hat{\rho}_{ij}(t) = \hat{\rho}_{ij}(0)e^{\frac{i}{\hbar}(E_i - E_j)t}$, which implies
\[
g_{uv,lj}^{<}(t_1, t) = i\langle \hat{\rho}_{ul}(0) \rangle_\delta_{ju} e^{\frac{i}{\hbar}(E_u - E_v)(t_1 - t_0)e^{-iEt_0}/h}.
\]
We wish to obtain a lesser Green’s function that only depends on a time difference, making the Fourier transform of the object straightforward. Similarly, the greater Green’s function is
\[
g_{uv,lj}^{>}(t_1, t) = -i\langle \hat{\rho}_{uj}(0) \rangle_\delta_{el} e^{\frac{i}{\hbar}(E_u - E_v)(t_1 - t_0)e^{-iEt_0}/h}.
\]
From the greater and the lesser Green’s functions we can compute the retarded and advanced ones as
\[
g_{uv,lj}^{r}(t_1, t) = -i\theta(t_1 - t) e^{\frac{i}{\hbar}(E_u - E_v)(t_1 - t_0)e^{-iEt_0}/h} \times (\langle \hat{\rho}_{uj}(0) \rangle_\delta_{el} + \langle \hat{\rho}_{ul}(0) \rangle_\delta_{ju}) e^{iEt_0/h}
\]
\[
g_{uv,lj}^{a}(t_1, t) = i\theta(t - t_1) e^{\frac{i}{\hbar}(E_u - E_v)(t_1 - t_0)e^{-iEt_0}/h} \times (\langle \hat{\rho}_{uj}(0) \rangle_\delta_{el} + \langle \hat{\rho}_{ul}(0) \rangle_\delta_{ju}) e^{iEt_0/h}.
\]
Considering also the isolated Green’s functions with times and indexes exchanged (see Eqs. (45) and (46)), and taking into account again the uncoupled equation of motion one can write
\[
\Lambda_{ij,\alpha\sigma}(t) = \frac{1}{2\pi} \sum_{nn'} e^{i(n' - n)\omega t} \sum_{uv} \lambda_{uv\sigma}^* \times
\]
\[
\left[ (\rho_{ul}(t)\delta_{ju} + \rho_{uj}(t)\delta_{el}) \int_{-\infty}^{+\infty} d\varepsilon \frac{\delta}{\varepsilon - \Delta_{uv}/h + i0^+} + 2\pi i\rho_{uj}(t)\delta_{el} \int_{-\infty}^{+\infty} d\varepsilon \delta \left( \varepsilon - \frac{\Delta_{uv}}{h} \right) \Sigma_{\alpha\sigma,nn'}^a(\varepsilon - n\omega) \right],
\]
where we already Floquet-Fourier transformed the expression. Moreover, $\Lambda_{\alpha\sigma,ij}$ is
\[
\tilde{\Lambda}_{\alpha\sigma,ij}(t) = \frac{1}{2\pi} \sum_{nn'} e^{-i(n' - n)\omega t} \sum_{uv} \lambda_{uv\sigma} \times
\]
\[
\left[ (\rho_{uj}(t)\delta_{el} + \rho_{ul}(t)\delta_{ju}) \int_{-\infty}^{+\infty} d\varepsilon \frac{\delta}{\varepsilon - \Delta_{uv}/h + i0^+} + 2\pi i\rho_{ul}(t)\delta_{ju} \int_{-\infty}^{+\infty} d\varepsilon \Sigma_{\alpha\sigma,nn'}^r(\varepsilon - n\omega) \delta \left( \varepsilon - \frac{\Delta_{uv}}{h} \right) \right].
\]
With Eqs. (52) and (53) one can write Eq. (22) identifying the Floquet-Fourier rate components as
\[
\Gamma_{\alpha\sigma,nn'}(\omega) = \frac{1}{2\pi} \left( \sum_{\alpha\sigma} \lambda_{\sigma\alpha\sigma} \lambda_{\alpha\sigma}^* \int_{-\infty}^{+\infty} d\varepsilon \frac{1}{\varepsilon - \Delta_{ju}/h + i0^+} \Sigma_{\alpha\sigma,nn'-n}(\varepsilon - n\omega) \right.
\]
\[
+ \sum_{\alpha\sigma} \lambda_{\sigma\alpha\sigma} \lambda_{\alpha\sigma}^* \int_{-\infty}^{+\infty} d\varepsilon \left[ 2\pi i\delta(\varepsilon - \Delta_{uj}/h) \Sigma_{\sigma\alpha,nn'}^r(\varepsilon - n\omega) + \frac{\delta}{\varepsilon - \Delta_{uj}/h + i0^+} \right] \left. \Sigma_{\alpha\sigma,nn'-n}(\varepsilon - n\omega) \right),
\]
and
\[
\tilde{\Gamma}_{\alpha\sigma,nn'}(\omega) = \frac{1}{2\pi} \left( \sum_{\alpha\sigma} \lambda_{\sigma\alpha\sigma} \lambda_{\alpha\sigma}^* \int_{-\infty}^{+\infty} d\varepsilon \frac{1}{\varepsilon - \Delta_{ju}/h + i0^+} \Sigma_{\alpha\sigma,nn'-n}(\varepsilon - n\omega) \right.
\]
\[
+ \sum_{\alpha\sigma} \lambda_{\sigma\alpha\sigma} \lambda_{\alpha\sigma}^* \int_{-\infty}^{+\infty} d\varepsilon \left[ \frac{\delta}{\varepsilon - \Delta_{uj}/h + i0^+} + 2\pi i\delta(\varepsilon - \Delta_{uj}/h) \Sigma_{\alpha\sigma,nn'-n}(\varepsilon - n\omega) \right] \left. \Sigma_{\alpha\sigma,nn'-n}(\varepsilon - n\omega) \right).\]

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