Spin-orbit interaction induces charge beatings in a lightwave-STM single molecule junction

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Recent lightwave-STM experiments have shown space and time resolution of single molecule vibrations directly on their intrinsic length and time scales. We address here theoretically the electronic dynamics of a copper-phthalocyanine in a lightwave-STM, explored within a pump-probe cycle scheme. The spin-orbit interaction in the metallic center induces beatings of the electric charge flowing through the molecule as a function of the delay time between the pump and the probe pulses. Interference between the quasi-degenerate anionic states of the molecule and the intertwined dynamics of the associated spin and pseudospin degrees of freedom are the key aspects of such phenomenon. We study the dynamics directly in the time domain within a generalized master equation approach.

I. INTRODUCTION

Spin-orbit interaction (SOI), the relativistic phenomenon which locks the spin and orbital degrees of freedom, is key in the emerging field of molecular spintronics [1]. It improves our capabilities to read, write and control spin states. It is therefore of utmost importance to gain a rigorous understanding and a precise control of SOI on the level of the microscopic building blocks of condensed matter themselves.

One may consider a gedanken experiment and observe what happens when a single electron is injected into one individual molecule. The electron is subject to the spin-orbit interaction and, at the same time, it exchanges energy with the local environment. Generally, extremely short lifetimes of the electronic spin state are expected. The ideal experiment would hence access electronic dynamics simultaneously on the atomic length scale and on time scales as short as femtoseconds. Such an ultimate experiment, fully resolving the dynamics of individual spins in space and time, can actually be implemented based on the latest breakthroughs of scanning tunnelling microscopy (STM) and ultrafast photonics [2, 3]. We address in this work its theoretical simulation.

Imaging, spectroscopy, and manipulation with atomic resolution has been achieved with steady state STM. Such experiments have provided unique insights into the equilibrium electronic states of molecules [4–9]. Resolving dynamics directly in the time domain, however, requires excitations to be confined to a short time window. An all-electronic pump-probe scheme has been realized in the seminal work by Loth and co-workers [10]. They achieved a direct observation of the relaxation of individual spins on the atomic length scale and the nanosecond timescale. A time resolution up to a few picoseconds has been progressively reached by optical means [11–13]. In parallel, ultrafast photonics has started to explore processes on time scales faster even than a single cycle of light. Thus, it became possible to stir electronic motion directly via the oscillating carrier wave of tailored light pulses – a principle often dubbed “lightwave electronics”.

Cocker et al. combine in [2] for the first time THz lightwave electronics with scanning tunnelling microscopy to initiate and monitor the center of mass oscillations of an individual molecule on the atomic length and sub-picosecond time scale. THz pulses act in their experiments analogously to voltage pulses in the all-electronic pump-probe experiments of [10], but they access much shorter timescales.

In our theoretical investigation, we propose a pump probe scheme to initiate and observe the SOI induced dynamics on a copper phthalocyanine (CuPc) molecule
The probe pulse overcomes a threshold. The first pulse brings CuPc, due to interference, into a superposition of many-body states. The dynamics of CuPc is clearly of fundamental importance in our proposed scheme by the interference effects associated to interacting nanojunctions with quasi orbital degeneracy, [14–17] recently observed in suspended CNTs [18]. CuPc does exhibit orbital degeneracy, protected by symmetry, and the pump pulse brings the molecule from its thermal equilibrium into a coherent superposition of the quasi-degenerate many-body states which blocks the current. The resulting electrical dark state is characterized by a well defined pseudospin, which, during the delay time, exhibits precession and beating dynamics under the influence of the SOI.

The average charge flowing through the STM junction during the probe pulse critically depends on the state reached by the molecule at the beginning of this second pulse. The closer is the molecule to the dark state, the lesser current can flow. Thus, the SOI induced dynamics leaves its fingerprints in the average charge per pump-probe cycle collected at the tip.

We calculate the transport characteristics of this driven and interacting single-molecule junction directly in the time domain, by means of a generalized master equation for the reduced density matrix of the molecule. Two complementary approaches to driven transport have been taken in the literature: approximated methods adapted to the parameter configuration of specific systems or numerically exact methods.

Prominent members of the first class are the Keldysh [19, 20] and scattering approaches [20, 21] to driven systems or quantum master equations [20, 21] that are especially suited for molecules with weak coupling to the leads. In the presence of a time-dependent driving field the energy is no longer a conserved quantity, and the evaluation of the time evolution operator becomes a nontrivial task. Simplifications are possible for time-periodic perturbations, allowing the use of Floquet theory [22]. Hence, to reduce complexity, most of the theoretical works so far have considered driven molecular bridges either in a single particle approximation [23–26] or in extremely simplified interacting models [20, 27, 28].

The second class of methods comprises numerically exact approaches: no perturbation parameter is introduced here, at a price of making these methods numerically extremely demanding. Because of this, electron-electron interactions and driving are considered for very simplified models of the molecular bridge [29, 30]. Recently, a quantum master equation approach has been derived for a driven interacting molecular bridge, with arbitrary shape of the driving field [31, 32].

We derive the quantum master equation for our system in the Markov approximation, relying on the fast relaxation of the electronic correlations in the metallic leads. We treat both the coupling to the leads as well as the SOI perturbatively and assume an adiabatic limit with respect to the driving speed. Yet the dynamics of CuPc is non-adiabatic, due to the matching of the time scales for the tunnelling events and the SOI induced precession. Moreover, we investigate also the influence of the Lamb shift correction to the coherent dynamics of the molecule. Such a contribution derives from the virtual electronic fluctuations between the molecule and the metallic leads. Due to the orbital degeneracies, it plays a significant role in the time evolution of the system, mainly during the time lapse between the two laser pulses.

The modelling of the Coulomb interaction and the SOI on the CuPc is clearly of fundamental importance in our transport calculations. Spin orbit coupling is known to be essential, in combination with the configuration of the non-magnetic component (organic ligand), in establishing the magnetic anisotropy in high-spin molecular magnets [33]. Effective spin Hamiltonians are commonly used to describe this anisotropy, and usually capture the low-energy properties of these systems well [33, 34]. Such effective Hamiltonians have been derived microscopically for the widely studied molecular magnets like Fe₈, Fe₄ and Mn₁₂ [35]. We have explicitly investigated long-range and short-range electron-electron correlation effects in CuPc [36]. By adding the SOI to our analysis,
we obtained a magnetic anisotropy which can in turn be captured by an effective spin Hamiltonian [37].

In general, the accurate calculation of the many-body properties of metalorganic molecules is a highly non-trivial task since the number of atomic constituents is large enough for exact diagonalization to be impossible, while standard density-functional schemes have difficulties in capturing short-ranged electron-electron correlations [35]. In order to reduce the size of the many-body Fock space, we use a basis of frontier molecular orbitals as the starting point to include electronic correlations and construct a generalized Hubbard Hamiltonian [36], an approach similar to the one presented in [35].

The paper is structured as follows: in Section II we first introduce the model Hamiltonian for CuPc, with focus on the low energy spectrum and eigenstates of the neutral and ionic molecule. The full description of the lightwave-STM is given in Section IIIB, with particular emphasis on the form of the tunnelling matrices. Moreover, in Section IIC we derive the generalized master equation for the reduced density matrix (RDM) and give the formula for the evaluation of the current in terms of this matrix. The latter is parametrized in Section IID by means of the product operator basis for the Liouville space. The intricate dynamics of the molecule during the pump pulse are described in Section III, introducing, step by step, first the tunnelling dynamics, then the influence of the SOI and finally the Lamb shift contribution to the state preparation. Free evolution and read out are discussed in Section IV. We concentrate on the pseudospin beatings revealing the intertwined dynamics of the spin and orbital degrees of freedom. Finally, we discuss the read-out mechanism implemented by the probe pulse. Concluding remarks and perspectives are given in Section V.

II. MODEL AND TRANSPORT THEORY

We introduce first the many-body Hamiltonian of the molecule under investigation and highlight the interplay of exchange and spin-orbit interaction in the characterization of its low energy eigenstates.

A. Copper phthalocyanine

Copper-phthalocyanine (CuPc) is a metalorganic compound with $D_{4h}$ symmetry consisting of an organic ligand surrounding a copper atom (see Fig. 1). We model the molecule with the Hamiltonian

$$H_M = H_{SP} + V_{ee} + H_{SOI} = H_0 + H_{SOI},$$

(1)
distinguishing the single particle $H_{SP}$, the electron-electron interaction $V_{ee}$ and the spin-orbit interaction $H_{SOI}$ component, respectively. The spin orbit interaction is treated perturbatively, due to its smaller energy scales as compared to the ones of $H_0$. We are interested into

the low energy states with the molecule being at most two times negatively charged ($\text{CuPC}^{2−}$). With reference to the interacting model derived by Siegert et. al [36, 37] we project the different terms of Eq. (1) on the many-body basis constructed with all possible occupations of four frontier orbitals (see Fig. 3). Listed with increasing single particle energy, these are, respectively, the singly occupied molecular orbital (SOMO or simply $S$ in the following), the highest occupied molecular orbital ($\text{HOMO}$ or $H$) and the two degenerate lowest unoccupied molecular orbitals (LUMOs). The latter are degenerate and thus admit different representations. We have chosen in Fig. 3 the one with real valued wave functions labelled $L_{xz}$ and $L_{yz}$ to recall their symmetry, the same of the atomic d-shell orbitals $d_{xz}$ and $d_{yz}$, with respect to the $D_{4h}$ group. The degenerate real LUMOs can be brought in their complex, rotationally invariant, form

$$|L_{\pm}\rangle = \frac{1}{\sqrt{2}}( |L_{xz}\rangle \pm i |L_{yz}\rangle ),$$

(2)

which will also be used in our discussions. The single particle Hamiltonian and the Coulomb interactions have, in the basis of the frontier orbitals, the generic form

$$H_0 = \sum_i \epsilon_i n_i + \frac{1}{2} \sum_{ijkl \sigma \sigma'} V_{ijkl} d_{i\sigma}^\dagger d_{j\sigma'}^\dagger d_{k\sigma'} d_{l\sigma},$$

(3)

where $i,j,k,l = S, H, L+, \text{ and } L−$, while $\sigma$ represents the spin and $n_i = d_{i\sigma}^\dagger d_{i\sigma}$ is the number operator for the $i$th molecular orbital. The single particle energies obtained from a tight binding calculation and renormalized by a crystal field correction [36, 37] are $\epsilon_S = −10.17 \text{ eV}$, $\epsilon_H = −9.87 \text{ eV}$, $\epsilon_{L\pm} = −8.87 \text{ eV}$. All Coulomb integrals $V_{ijkl}$ have been included in the numerical evaluation of $H_M$. 

![Figure 3](image-url) - Isosurfaces of the four frontier orbitals: SOMO, HOMO and the real valued LUMOs. The color indicates the sign of the wavefunction at the isosurface. Green corresponds to a positive, purple to a negative sign.
For the scope of the discussion, we only recall the values of the Hubbard energy of the different orbitals $U_i = V_{iiii}$, i.e. $U_S = 11.4$ eV, $U_H = 1.8$ eV and $U_{L\pm} = 1.8$ eV, and the exchange coupling between the SOMO and LUMO $J = V_{SLLS} = 9$ meV. The large difference between the Hubbard energy of the SOMO with respect to the ones of the HOMO justifies the single occupation of the first in the neutral ground state of the molecule despite the ordering of the single particle orbital energies, which sees the SOMO below the HOMO level. We refer to [37] for the complete table of the Coulomb integrals.

The SOI Hamiltonian for the molecule is the superposition of the atomic ones

$$ H_{SOI} = \sum_\alpha \xi_\alpha \vec{l}_\alpha \cdot \vec{s}_\alpha, \quad (4) $$

where $\alpha$ is a collective index which runs over all atoms and shells, $\vec{l}_\alpha$ is the corresponding angular momentum operator and $\vec{s}_\alpha$ is the spin operator. We concentrate, though, only on the $d$-shell of the copper atom, which carries by far the largest spin orbit coupling $\xi$. Projecting this contribution into the basis of the frontier orbitals yields eventually

$$ H_{SOI} = \lambda_1 \sum_{\tau = \pm} \tau \left( d_{\tau\tau\uparrow}^\dagger d_{\tau\tau\uparrow} - d_{\tau\tau\downarrow}^\dagger d_{\tau\tau\downarrow} \right) + \lambda_2 \left( d_{\Sigma\uparrow}^\dagger d_{\Sigma\downarrow} + \text{h.c.} \right), \quad (5) $$

with the effective SOI parameters $\lambda_1 = 0.47$ meV and $\lambda_2 = 6.16$ meV. The size of the effective SOI parameters with respect to the bare one of the copper $d$-shell $\xi_{Cu} \approx 100$ meV [38] reflects the relatively low weight of the LUMOs on the copper atom, see Fig. 3.

The electronic transitions induced by the tunnelling events between the leads and the molecule involve the many-body eigenstates of the molecule. In order to retain correlation effects, we calculate them via the exact diagonalization of the Hamiltonian in Eq. (1) within the full configuration space of the four frontier orbitals depicted in Fig. 3. We focus here on the neutral and anionic low energy states, within an energy range of a few meV. Only these states will play a role in our transport calculations. The eigenstates of the Hamiltonian in Eq. (1) are linear combinations of several Slater determinants which we fully retain in the numerical calculations. The admixtures are though very small and we neglect them in the analytical description of the eigenstates presented below. To this end, it is useful to define a state $|\Omega\rangle = d_{H\uparrow}^\dagger d_{H\downarrow}^\dagger |0\rangle$, and to express the energy eigenstates in terms of $|\Omega\rangle$.

The neutral ground state is a spin degenerate doublet with a predominant contributions of the states

$$ |D^\uparrow\rangle = d_{\uparrow\uparrow}^\dagger |\Omega\rangle, \quad |D^\downarrow\rangle = d_{\downarrow\downarrow}^\dagger |\Omega\rangle, \quad (6) $$

where we observe the characteristic unpaired spin in the SOMO. The first excited neutral energy level lies about 0.8 eV above the ground state [36] and thus we do not consider it in our calculations.

The analysis of the anionic spectrum moves from the identification of three distinct energy scales in the system, i.e. the direct Coulomb interaction ($U$, for simplicity), the exchange coupling ($J$) and the SOI parameters ($\lambda$), with the clear separation $U > J > \lambda$. The degeneracy, as well as the spin of the ground state is influenced by this three energy scales.

Only considering the direct Coulomb interactions between the molecular orbitals would yield the degenerate anionic ground state

$$ |4\tau\sigma\sigma'\rangle = d_{S\sigma}^\dagger d_{L\tau\sigma'}^\dagger |\Omega\rangle, \quad (7) $$

with the eight-fold degeneracy ensured by the combination of the orbital degree of freedom $\tau$, the spin degree of freedom spin $\sigma$ in the SOMO and $\sigma'$ in the LUMO. The high Hubbard energy of the SOMO is responsible for the occupation of a LUMO, instead of the double occupation of the SOMO, in the anionic state.

By unitary transformation we can express these states also as two sets of singlets and triplets

$$ |S_\tau\rangle = \frac{1}{\sqrt{2}} \left( d_{S\uparrow}^\dagger d_{L\tau\downarrow}^\dagger - d_{S\downarrow}^\dagger d_{L\tau\uparrow}^\dagger \right) |\Omega\rangle, \quad |T^+_\tau\rangle = d_{S\uparrow}^\dagger d_{L\tau\uparrow}^\dagger |\Omega\rangle, \quad (8) $$
$$ |T^0_\tau\rangle = \frac{1}{\sqrt{2}} \left( d_{S\uparrow}^\dagger d_{L\tau\downarrow}^\dagger + d_{S\downarrow}^\dagger d_{L\tau\uparrow}^\dagger \right) |\Omega\rangle, \quad |T^-_\tau\rangle = d_{S\downarrow}^\dagger d_{L\tau\downarrow}^\dagger |\Omega\rangle, $$

where the two sets, labelled by the angular momentum $\tau$, arise due to the degenerate LUMOs. We identify the orbital degree of freedom in the subscript, while the superscript of the triplet states gives the value of $S_\tau$. The the exchange interaction ($\propto J$) lifts the degeneracy between the triplet and singlet states, with the triplets becoming the new (still orbitally degenerate) ground state. Eventually, the triplet state degeneracy is partially lifted by the SOI which leads us to the actual eigenstates of

![FIG. 4. Low energy spectrum of CuPc. With only Coulomb interaction the spectrum is eightfold degenerate. Exchange coupling splits the triplet and singlet states. SOI further lifts the degeneracy of the triplet states. Adapted from [37].](image-url)
the molecule, ordered from lowest to the highest in energy \( |T^+_{-1}⟩, |T^0_{+1}⟩, |T^0_{-1}⟩, |T^+_{+1}⟩, |T^0_{0}⟩, |T^+_{-1}⟩ - |T^0_{-1}⟩ \) and \( |T^+_{+1}⟩ + |T^0_{-1}⟩ \). Time reversal symmetry ensures the robustness of the singlets orbital degeneracy under the perturbation of the SOI: they only experience a slight downshift in energy of \( \approx 4 \times 10^{-2} \text{meV} \).

The anionic low energy spectrum and its relation to the different energy scales associated to the molecule is depicted in Fig. 4. The splitting of \( \approx 1 \text{meV} \) of the triplet states due to the SOI is comparable, as we will discuss in the next section, to the energy broadening introduced by the coupling to the tip and substrate, thus making these states quasi-degenerate, an essential requirement for the interference effects [17, 18, 39, 40] underlying the preparation and read-out protocols proposed here.

### B. Lightwave-STM

We describe the STM nanojunction in Fig. 1 by means of the system-bath Hamiltonian

\[
H = H_M + H_{IC} + H_T + H_L,
\]

with the many-body molecular Hamiltonian \( H_M \) introduced in the previous section. The leads and the insulating thin film are responsible of polaronic and image charge effects[41–43] which renormalize the energies of the charged states. We simply account for this renormalization via the term

\[
H_{IC} = -\delta_{IC}(N - 3)^2,
\]

with \( N \) the operator counting the total number of electrons occupying the frontier orbitals (three in the neutral state), and \( \delta_{IC} = 0.32 \text{eV} \). This parameterization is obtained by fitting our model to experimental transport gaps obtained from differential conductance measurements of CuPc on substrates with different work functions [36]. The molecule exchanges particles with the leads via a weak tunnelling coupling. The state of the molecular junction in thermal equilibrium is thus obtained by considering a grand canonical ensemble with the equilibrium chemical potential of the leads. We choose such chemical potential to be \( \mu_0 = -4 \text{eV} \) which keeps the molecule in its anionic state, i.e. with one additional electron, as shown schematically in Fig. 5.

The leads are non-interacting Fermi seas with the Hamiltonian

\[
H_L = \sum_{\text{tip},k_\sigma}\epsilon_k c_{k\sigma}^\dagger c_{k\sigma},
\]

where \( \eta \) labels the tip or substrate and \( c_{k\sigma} \) destroys an electron with momentum \( k \) and spin \( \sigma \) in the lead \( \eta \). The spectrum of the lead is rigidly shifted by the applied bias across the junction. The same happens to the corresponding chemical potential \( \mu_\eta(t) = \mu_0 + \alpha_\eta V_{bias}(t) \), thus ensuring the charge neutrality of the lead. Conventionally, we assume the energy levels of the molecule to remain unchanged during the pulse, while the tip and substrate levels are shifted in opposite directions [44]. In our set up the bias drops asymmetrically across the junction and the parameters \( \alpha_\eta \), which depends on the tip height, are estimated in \( \alpha_{\text{tip}} = -0.54 \) and \( \alpha_{\text{sub}} = 0.08 \), according to electrostatic considerations [36]. The residual potential drop across the molecule is compensated by a polarization of the molecule [45] whose influence on the molecular eigenstates we neglect in this work.

It is the laser pulse impinging on the molecule to generate, in the lightwave-STM, a bias pulse across the junction [2, 3]. Consequently, the tip and substrate chemical potentials acquire a time dependence which drives the system dynamics. The many-body eigenenergies together with the potential drop fractions \( \alpha_\eta \) at the different leads set the thresholds biases at which new tunnelling events can occur [16], with the sensitivity set by the temperature.

In first approximation we give much more importance to the time interval of an open transition as to the exact shape of the bias pulse. We thus replace in our simulations the bias pulses by (smoothed) square pulses.

The coupling between the molecule and the leads is given by the tunneling Hamiltonian

\[
H_T = \sum_{\text{tip},k\sigma} t_{\sigma_{\eta k\sigma}}^\eta c_{\eta k\sigma}^\dagger d_{\sigma} + \text{h.c.},
\]

with \( \{t_{\sigma_{\eta k\sigma}}^\eta\} \) the set of tunneling amplitudes. The latter are, according to the tunnelling theory of Bardeen [46], the overlap integrals between the leads states (labelled here by momentum \( k \) and spin \( \sigma \)) and the molecular orbitals (\( \eta = S, H, L\pm \) and the same spin \( \sigma \)). They encode the geometry of the contact, which, in a STM junction...
is very asymmetric, with the atomically flat substrate opposed to the extremely sharp tip. This qualitative difference between the two contacts is clearly reflected into the single particle tunnelling rate matrices. The latter extend the concept of tunnelling rates between energy levels in presence of degeneracies in the spectrum of the system [18, 47]. They are defined on the single particle basis of the molecule as

$$\Gamma_{i\sigma,j\sigma'}(E) = \frac{2\pi}{\hbar} \sum_k (t_{ik\sigma})^* t_{jk\sigma'}^\eta \delta(\epsilon_k^\eta - E).$$

In [47] we calculate explicitly the tunnelling rate matrices for a benzene molecule, starting from microscopic models for the leads. In this work we opt for a simplified form, still capturing, though the fundamental symmetries of the problem. In particular, the tip’s tunnelling rate matrix must yield the topography of the molecules of the problem. To this end, in accordance with Chen’s derivative rule [48] for an $s$-symmetric tip, the tunnelling matrix assumes, for the generic element

$$\Gamma_{i\sigma,j\sigma'}(r_{tip}) = \gamma_0 \psi_i^\eta(r_{tip}) \psi_j^\eta(r_{tip}) \delta_{\sigma\sigma'},$$

where $\gamma_0$ is proportional to the local density of states of the tip and we approximate it to a constant in the energy range relevant for our calculations (wide band limit). Moreover, we estimate its value from a typical constant current set point of STM experiments on CuPc together with the corresponding topographical images [49]. At a distance of 3 Å from the horizontal symmetry plane of the molecule, we obtain a maximal tunnelling rate to the LUMO orbitals $\max_{r_{tip}} \Gamma_{\sigma\sigma'}(r_{tip}) = 0.2$ meV. The localized tip breaks, in general, the rotational symmetry of the molecule and the presence of off-diagonal terms in the associated tunnelling matrix, when written in the energy and angular momentum basis. The positivity of the rate matrix is instead guaranteed, in our approximation, by the fact that the tip tunnelling matrix has by construction only a single non zero eigenvalue, while its trace is proportional to the sum over the orbital densities calculated at the tip position. The frontier orbitals S, H and L± belong to different irreducible representations of the $C_{4v}$ symmetry group characterizing CuPc on the NaCl substrate. The substrate tunnelling rate matrix is thus diagonal. The microscopic proof of this statement is found in [47] where the analogous case of a benzene molecule has been analyzed in detail. For simplicity we reduce here the substrate tunnelling rate matrix to the form

$$\Gamma_{\text{sub}}_{i\sigma,j\sigma'} = \Gamma_0 \delta_{\sigma\sigma'},$$

thus neglecting the differences between the molecular orbitals. The diagonal components associated to the two LUMOs are identical due to time reversal symmetry. Moreover, the tunnelling events connecting the neutral and the anionic low energy states, considered here, mostly involve the addition or removal of an electron in the LUMOs and justify, for the sake of simplicity the approximation in Eq. (15). The overall strength of the tunnelling coupling to the metallic substrate has been fixed in accordance to DFT calculations with a monolayer of NaCl on Cu(111) [5] and set to 0.5 meV.

C. Transport theory

The electronic transport calculation reported in this work is based on the STM theory for single molecules on thin insulating films presented in [47]. We proceed in the framework of a generalized master equation, which naturally allows for the treatment of strong electronic correlations on the molecule [8, 50–52]. The latter plays a crucial role in STM on thin insulating film, as the presence of the insulator hinders the screening associated to the hybridization with the metallic substrate and enhances the specific features of the pristine molecule [5, 7, 8, 53]. The starting point is the Liouville-von Neumann (LvN) equation for the full density matrix

$$\dot{\rho}_{\text{tot}} = -\frac{\hbar}{2i} [H(t), \rho_{\text{tot}}],$$

where, due to the laser-induced bias pulses, the explicit time dependence in the Hamiltonian has been highlighted. As we treat the tunneling perturbatively, it is convenient to write the LvN equation in the interaction picture $\dot{\rho}_{\text{tot}}^I = -\frac{\hbar}{2i} [H^I(t), \rho_{\text{tot}}^I]$. Moreover, we are primarily interested in the dynamics of the molecule, thus we aim at the equation of motion for the reduced density matrix (RDM), obtained by tracing out the leads degrees of freedom $\rho = \text{Tr}_L \{\rho_{\text{tot}}\}$. The initial time factorization for the density operator into a molecule and a leads component $\rho_{\text{tot}}(t_0) = \rho_M(t_0) \otimes \rho_L(t_0)$ allows one to derive the following integro-differential equation of motion for the reduced density matrix

$$\dot{\rho}^I(t) = \int_{t_0}^t K^{(2)}_{I}(t,t')\rho^I(t')dt',$$

valid to second order in the tunnelling coupling, with the interaction picture propagation kernel

$$K^{(2)}_{I}(t,t') = -\frac{\hbar^2}{2} \text{Tr}_L \left\{ [H^I_I(t), [H^I_I(t'), \rho^I_I(t') \otimes \rho_L(t_0)]] \right\}.$$  

In Eq. (17) the dynamics of the RDM at time $t$ can be determined only with the knowledge of the RDM at all previous times, starting at the initial time $t_0$, thus showing a memory effect. The propagator kernel vanishes, though, for $t - t' \to \infty$, due to its proportionality to the lead correlator

$$F(t,t';\eta) = \sum_{k\sigma} \text{Tr}_L \left\{ c_{\eta k\sigma, 1}^\dagger (t) c_{\eta k\sigma, 1} (t') \rho_L(t_0) \right\}. $$

The time scale $\tau_{rel}$ of its exponential decay, is given, for a thermal bath of non interacting fermions, by $\tau_{rel} \approx \hbar \beta$.
where $\beta = (k_B T)^{-1}$ is the inverse thermal energy. The speed in the dynamics of the RDM is instead measured by $\hbar \Gamma$, the overall level broadening introduced by tunnelling and by a third time scale associated to the variation speed of the bias pulse $\tau_{\text{pulse}}$. We concentrate on the weak-coupling, adiabatic limit $1/\Gamma \approx \tau_{\text{pulse}} \gg \tau_{\text{rel}}$. Similarly to [24], we obtain, from Eq. (17), the time local propagator kernel

$$\rho'(t) = \frac{-1}{\hbar^2} \int_0^\infty dt' \text{Tr}_L \left\{ [H_T^l(t), [H_T^l(t-t'), \rho'(t) \otimes \rho_L(t_0)]] \right\}. \tag{20}$$

Moreover, vibrations in the contacts reduce the relaxation time of the electronic correlator, by introducing additional dissipative channels for the electronic excitations, as was recently discussed in [54, 55]. Thus the range of validity of our approximation should also accommodate the cryogenic temperatures and tunnelling couplings of the lightwave-STM experiments [2, 3].

In support of our argument we notice, moreover, that the differential conductance peaks in STM experiments on thin insulating films [5, 7, 53, 56] show a gaussian profile and a width clearly much larger than both the thermal energy $k_B T$ and the tunnelling induced broadening $\hbar \Gamma$. The role of substrate optical phonons in the explanation of such anomalous spectral broadening of the conductance has been demonstrated [57] and also controlled by changing the insulating layer from a NaCl to a RbI or Xe one [56].

By evaluating the time integrals in Eq. (20) and converting the equation to the Schrödinger picture we finally obtain the desired GME

$$\dot{\rho}(t) = [\mathcal{L}_M + \mathcal{L}_T(t) + \mathcal{L}_{\text{LS}}(t)]\rho(t). \tag{21}$$

The first term $\mathcal{L}_M$ describes the coherent evolution of the isolated molecule. For later convenience we express it in the Liouville superoperator formalism

$$\mathcal{L}_M = -\frac{i}{\hbar} \sum_{\alpha = \pm 1} \alpha \mathcal{H}_{M,\alpha}, \tag{22}$$

where $\mathcal{H}_{M,\alpha}$ acts on the following density operator as, $\mathcal{H}_{M,\alpha} \rho := H_M \rho$ and $\mathcal{H}_{M, -\rho} \rho = \rho H_M$.

The tunnelling coupling between the system and the leads treated in the lowest non vanishing perturbative order is responsible of the two additional terms in Eq. (21). We refer to them as the tunnelling and the Lamb shift Liouvillean, respectively. In the superoperator notation, they read

$$\mathcal{L}_T(t) = -\frac{1}{2} \sum_{\alpha_1,\alpha_2} \sum_{nm} \sum_{pq} \alpha_1 \alpha_2 \Gamma_{nm}^{\eta,p} \mathcal{D}^\eta_{n,m} f^{(\alpha_1,p)}(i\hbar p L_0) \mathcal{D}^p_{m,\alpha_1}, \tag{23}$$

and

$$\mathcal{L}_{\text{LS}}(t) = -\frac{i}{2\pi} \sum_{\alpha} \sum_{nm} \sum_{pq} \alpha \Gamma_{nm}^{\eta,p} \mathcal{D}^\eta_{n,m} \mathcal{D}^p_{m,\alpha} (i\hbar p L_0) \mathcal{D}^p_{m,\alpha}. \tag{24}$$

The tunnelling and the Lamb shift Liouvillean both depend on time via the lead chemical potential $\mu_\alpha(t)$ which shifts the argument of the Fermi function $f^\eta_\alpha(\epsilon) := \left\{ 1 + e^{\beta \left( \epsilon - \mu_\alpha(t) \right)} \right\}^{-1}$ and of the principal part function $p_\eta(\epsilon) = -\Re \psi \left\{ \frac{1}{2} + i\pi \left[ \epsilon - \mu_\eta(t) \right] \right\}$, the latter being defined via the real part of the digamma function $\psi$. The collective indices $n$ and $m$ fully identify the molecular orbital, while $p = \pm$ and $\bar{p} = -p$ distinguish in $\mathcal{D}^\eta_{n,m}$ the creation from the annihilation operator, associated respectively to $p = +1$ and $p = -1$. Notice, moreover, that $\Gamma_{n,m}^{-} = \Gamma_{n,m}^{0}$ and $\Gamma_{n,m}^{+} = \Gamma_{n,m}^{\eta}$. Analogously to the coherent Liouvillean presented above, the creation and annihilation operators are dressed with the Liouville index $\alpha$ which identifies from which side they act on the following operator.

Additionally, we only include in Eq. (23) and (24) the unperturbed Liouvillean of the system $\mathcal{L}_0 = -\frac{i}{2} \sum_{\alpha' = \pm 1} \alpha' \mathcal{H}_0 \alpha'$ in the calculation of $\mathcal{L}_T$ and $\mathcal{L}_{\text{LS}}$. The energy splitting $\delta \epsilon$ induced by the SOI is comparable to the level broadening $\hbar \Gamma$. We perform, however, a perturbation expansion up to first order in $\Gamma$ and therefore we must exclude terms proportional to $\hbar \delta \epsilon$ which are comparable to cotunnelling contributions $O(\Gamma^2)$ to the dynamics. This approach is equivalent to treating the problem in the singular coupling limit as discussed in [39, 58].

While the tunnelling events connecting many-body eigenstates with adjacent particle number are described by $\mathcal{L}_T$, the Lamb shift Liouvillean $\mathcal{L}_{\text{LS}}$ outlines the virtual transitions of electrons which preserve the particle number on the molecule, with the net result of renormalizing the coherent dynamics generated by the system Hamiltonian. In this sense it is possible to write the Lamb shift Liouvillean as a commutator with an effective system Hamiltonian $H_{\text{LS}}$.

The SOI induced evolution renormalized by the Lamb shift and the tunnelling are characterized by comparable time scales. They combine to yield a driven non adiabatic evolution of the system. The reduced density ma-
trix fully captures such dynamics. The proposed read-out mechanism to probe it, is the measurement of the average current flowing through the STM nanojunction due to repeated pump-probe cycles as a function of the delay time between the pulses. To this end we first calculate the time dependent reduced density matrix by solving the GME in Eq. (21) with a thermal initial condition. The latter is a reasonable assumption for long enough repetition periods of the pump-probe cycle. The current through the system is then obtained as

\[
\langle I(t) \rangle = \text{Tr}_M \left\{ \{ \mathcal{J}_n^+ (t) - \mathcal{J}_n^- (t) \} \rho(t) \right\},
\]

where the time dependent jump superoperators \( \mathcal{J}_n^\pm (t) \) refer to the tunnelling events to and from the lead \( n \) respectively. They read

\[
\mathcal{J}_n^+ (t) = \sum_{n,m} \Gamma_{n,m} D_{n,m,-} (i \hbar \mathcal{L}_0) D_{m,n,+},
\]

\[
\mathcal{J}_n^- (t) = \sum_{n,m} \Gamma_{n,m} D_{n,m,-} (i \hbar \mathcal{L}_0) D_{m,n,+},
\]

where the explicit time dependence is contained, as for the tunnelling and Lamb shift Liouvilleans, in the time dependent chemical potentials which shift the argument of the Fermi functions.

### D. Operator space

The density matrix \( \rho \) describing an \( n \)-dimensional Hilbert space is, in general, a \( n \times n \) Hermitian, positive definite matrix, thus parameterized by \( n^2 \) real numbers \[59\]. This number of parameters is the size of the Liouville (vector) space to which \( \rho \) belongs. By exploiting the notion of scalar product, also defined on Liouville spaces, we obtain, for any orthogonal basis set \( \{ B_i \} \), the expansion

\[
\rho = \sum_i \frac{\langle B_i | \rho \rangle B_i}{\langle B_i | B_i \rangle},
\]

with \( | \rho \rangle \) the vector notation for the density operator in Liouville space and the scalar product defined as \( \langle A | B \rangle = \text{Tr} \{ A^\dagger B \} \). Interestingly, the scalar product \( \langle B_i | \rho \rangle = \langle B_i \rangle \) is equivalent, for a basis of Hermitian operators, to the expectation value of the observable \( B_i \). Thus, the combination of Eqs. (20) for a suitable basis set and (27) translates the GME into a set of coupled linear differential equations for \( n^2 \) expectation values of system observables. Those equations give valuable information about the interplay of molecular observables and a more intuitive physical picture of the molecular dynamics with respect to the original GME.

As already discussed, we are interested into the coupled dynamics of the neutral ground state and of the low energy set of triplet and singlet anionic states. The corresponding density matrix consists of three separate blocks, as i) coherences between states with different particle number is forbidden in absence of superconducting correlations and ii) the energy splitting between the singlet and the triplet exceeds by far the tunnelling coupling, thus justifying the use of the secular approximation which neglects the fast oscillating coherences between singlet and triplet states.

The matrix block associated to the neutral, spin degenerate state can be expanded on the basis \( B^\dagger = \{ 1_2, \frac{S^x}{\sqrt{2}}, \frac{S^y}{\sqrt{2}}, \frac{S^z}{2} \} \), with \( \sigma_\alpha \) the Pauli matrices, to obtain

\[
\rho^d = \frac{p^d}{2} 1_2 + \langle \tau^d \rangle \cdot \sigma,
\]

where \( p^d \) is the population of the doublet neutral level and \( S^d_\alpha = \sigma_\alpha/2 \) is the matrix representation of the \( \alpha \) component of the spin operator in the doublet basis and vanishes elsewhere.

The orbitally degenerate singlet anionic states are treated analogously. The definition of a set of pseudospin operators \( \tau^s_\alpha = \sigma_\alpha/2 \) with \( \alpha = x, y, z \) leads to the analogous decomposition of the corresponding block in the density matrix

\[
\rho^s = \frac{p^s}{2} 1_2 + \langle \tau^s \rangle \cdot \sigma,
\]

where \( p^s \) is the total population of the singlet degenerate level. The most interesting sub-block is the one spanned by the triplet states. The triplet space is of the ten-dimensional space, neglecting the fast oscillating coherences between singlet and triplet states.

The corresponding density matrix consists of three separate blocks, as i) coherences between states with different particle number is forbidden in absence of superconducting correlations and ii) the energy splitting between the singlet and the triplet exceeds by far the tunnelling coupling, thus justifying the use of the secular approximation which neglects the fast oscillating coherences between singlet and triplet states.

As the Hilbert space is 3-dimensional, the associated Liouville space has dimension 9. Therefore, it is not enough to expand the corresponding density matrix in terms of the identity and the spin operators. Five additional operators are needed to complete a basis set. The spin quadrupole operators make the job

\[
S_{xz} = 2S_x S_z - S_x^2 - S_y^2,
S_{xy} = S_x S_y + S_z S_x,
S_{yz} = S_y S_z + S_x S_y,
S_{xz}^2 = S_x^2 - S_y^2,
S_{xy}^2 = S_x S_y + S_y S_x.
\]

\[31\]
Altogether we set up the following basis for the description of a spin 1 density matrix

$$\mathcal{B}^1 = \left\{ 1_3, S_x, S_y, S_z, S_{x^2}, S_{y^2}, S_{x^2y^2}, S_{xy^2} \right\}.$$  \hspace{1cm} (32)

By combining the two bases $\mathcal{B}^{1/2}$ and $\mathcal{B}^1$ we obtain a basis in which we can expand the density matrix for the triplet space

$$\mathcal{B}^T = \mathcal{B}^1 \otimes \mathcal{B}^{1/2}.$$  \hspace{1cm} (33)

The description of the orbitally degenerate triplet space requires more than just the population $\rho^i = \text{Tr} \{ \rho^i \}$ and expectation value of the separate spin (dipole and quadrupole) and pseudospin operators, calculated respectively as

$$\langle S_i^i \rangle = \text{Tr} \{ \rho^i (S_i \otimes 1_2) \},$$  \hspace{1cm} (34)

and

$$\langle \tau_\alpha^\alpha \rangle = \text{Tr} \{ \rho^i \left( 1_3 \otimes \frac{\sigma_\alpha}{2} \right) \},$$  \hspace{1cm} (35)

where $\rho^i$ is the triplet block of the density matrix, $S_i$ is one of the spin operators in $\mathcal{B}^1$ and $\sigma_\alpha$ one of the Pauli matrices. In general, also the mixed spin and pseudospin correlators

$$\langle S_i^i \tau_\alpha^\alpha \rangle = \text{Tr} \left\{ \rho^i \left( S_i \otimes \frac{\sigma_\alpha}{2} \right) \right\},$$  \hspace{1cm} (36)

must be taken into account. These mixed correlators play a crucial role in the description of SOI induced dynamics, in which spin and orbital evolution are intertwined and the equation of motion of the spin or pseudospin variables is coupled to the one of the correlators, since the latter do not factorize $\rho^i \langle S_i^i \tau_\alpha^\alpha \rangle \neq \langle S_i^i \rangle \langle \tau_\alpha^\alpha \rangle$, with $\rho^i$ the occupation of the triplet states.

III. INITIAL STATE PREPARATION

The pump laser pulse impinging on the molecule excites it out of its thermal equilibrium and is responsible for its initial state preparation. The evolution of the molecular many-body state during the preparing pulse is characterized by the interplay of several processes giving rise to a complex dynamics. To scrutinize the role of the different contributions, we examine the initial state preparation step by step. First we concentrate only on the interference effects associated to the tunnelling processes. In a second and third step we add the contributions of the SOI and the Lamb shift.

A. Tunneling dynamics

The fundamental mechanism underlying the initial state preparation of the CuPc is the interference blocking characterising nanojunctions with quasi-degenerate many-body spectrum and weakly coupled to the leads [14, 16, 17, 51]. This blockade, previously investigated only in the stationary limit, only arises when the applied bias voltage exceeds the threshold for triggering sequential tunnelling events and moreover unidirectional transport is induced through the junction (high bias limit).

For this reason, we first consider the STM junction under a constant over-threshold bias and analyze how the system achieves the stationary state, as shown in Fig. 6. The tip position is fixed at 3 Å above the horizontal symmetry plane of the molecule, in the vicinity of one of the lobes of the $L_{yz}$ orbital (compare Fig. 7 and Fig. 3). Moreover, we apply a (sample) bias of $V_b = -0.4$ V to the system and, at first, neglect the SOI and Lamb shift contribution to the dynamics. The RDM is thus governed by the differential equation $\dot{\rho} = \mathcal{L}_T \rho$, supplemented by the thermal initial condition $\rho(t_0) = \exp[-\beta (H_M - \mu_0 N)] / Z_G$ with $Z_G$ the grandcanonical partition function. The simulation (as also the others reported in this manuscript) has been performed at a temperature of $T = 30$ K. Initially the system has an essentially equal probability to be in any of the triplet anionic states, while the singlets and the neutral doublet are empty. Thermal fluctuations are, in fact, not strong enough to populate these states, as $E^t - E^s \gg k_B T$ and also $E^d - E^t + \mu_0 \gg k_B T$, being, $E^t$, $E^s$, and $E^d$ respectively the energy of the triplets, singlets and doublet levels, calculated for simplicity in absence of the SOI perturbation.

The bias, applied here from the beginning, is instead large enough to trigger transitions between the anionic triplets and the neutral doublet ground state with one electron tunneling from CuPc towards the tip. Therefore, as can be seen from the eigenvalues of the density
matrix plotted in Fig. 6 (a), at first the doublet gets populated. Soon, though, tunnelling of an electron from the substrate brings the molecule back to an anionic configuration in which, on average, both singlets and triplets are populated.

For a time lapse of a few picoseconds both the neutral and the anionic levels are populated and current flows through the molecule. Gradually some triplet states (three of them, in fact) and one singlet state act as probability sinks. Despite transitions to the neutral doublet remaining energetically available (the bias is kept constant, here), within approximately 4 ps the entire occupation probability is concentrated in the anionic state and the current is blocked. This evolution of the density matrix eigenvalues is the time resolved observation of the dark state formation theoretically predicted [14, 17, 40, 47] and recently observed in carbon nanotubes [18].

The more direct fingerprint of the interference blocking mechanism is represented, though, by the non-zero rates to the tip and substrate, respectively. Moreover we interpret this condition as pseudospin accumulation in a dipolar when the tip moves along the vertical arm of CuPc. Vice versa, the blocking state has mainly a singlet structure since in this region $\psi_{xz}$, the pseudospin wavefunctions of the real val-ued LUMOs depicted in Fig. 3. The over-threshold bias with enforced unidirectional transport implies that $f_{\text{tip}}^+(\epsilon_t)$, $f_{\text{tip}}^-(\epsilon_t)$, $f_{\text{sub}}^+(\epsilon_s)$ and $f_{\text{sub}}^-(\epsilon_s)$ are exponentially suppressed. Looking for the stationary solution of Eqs. (37), under those assumptions, we obtain the following conditions

$$\langle \tau^t \rangle = -\frac{1}{2} P_T p^t, \quad \langle \tau^s \rangle = -\frac{1}{2} P_T p^s, \quad (39)$$

which, when inserted into the equations for the popul-
tions, yield

$$\dot{p}^t = \sum_\eta \left[ 3 \Gamma^\eta f_\eta^+(\epsilon_t) \right] p^d - \Gamma^\text{sub} f_{\text{sub}}^-(\epsilon_t) p^t,$$

$$\dot{p}^s = \sum_\eta \left[ \Gamma^\eta f_\eta^+(\epsilon_s) \right] p^d - \Gamma^\text{sub} f_{\text{sub}}^-(\epsilon_s) p^s,$$

$$\dot{p}^d = \sum_\eta -\Gamma^\eta [3 f_\eta^+(\epsilon_t) + f_\eta^-(\epsilon_t)] p^d$$

$$+ \Gamma^\text{sub} f_{\text{sub}}^-(\epsilon_t) p^s + \Gamma^\text{tip} f_{\text{sub}}^-(\epsilon_t) p^t.$$  \quad (40)

The equations above do not contain any rate proportional to $f_{\text{tip}}^-(\epsilon_t/s)$, thus revealing how tunnelling events towards the tip are completely suppressed.

Thus, on a time scale fixed by the smallest between the tip and the substrate rates, the neutral state gets depopulated, $p^t + p^s = 1$, and the total pseudospin reads

$$\langle \tau \rangle = -\frac{1}{2} P_T.$$  \quad (41)

In close analogy to the spin valve problem [60] we interpret this condition as pseudospin accumulation in a direction antiparallel to the lead polarization $P_T$, with the formation of an electronic dark state. The molecule is, in this configuration, completely decoupled from the tip and thus, in the infinite time limit, the ratio between the populations of the singlet and the triplet is expected to reduce to the Boltzmann factor. This condition, though, is clearly not the one shown in Fig. 6, even after 15 ps. The steady state would be reached only over a much longer time scale, set by the depopulation rate of the singlet towards the substrate, which is strongly suppressed due to the Coulomb blockade on the molecule and the sign of the applied bias.

In Fig. 7 (a) and (b) we represent the different molecular states prepared by scanning with the tip over the molecule in terms of their pseudospin components. The maps are obtained by simulating an overthreshold bias pulse of the duration of 3 ps and by computing the pseudospin values corresponding to the end of the pulse. The system is not yet converged to the quasi-stationary configuration discussed above but is shows already clear signatures of the complete blocking state, as can be seen, for example in the reentrant doublet population in Fig. 6 (a). This choice of the pulse duration, will become clearer at a later stage when the role of the SOI will be considered. The pseudospin show a prominent dependence on the tip position which is explained by means of Eq. (41) and Eq. (38) in combination with Fig. 3.

CuPc has a roughly a cross shape. If the tip is placed along the horizontal arm with respect to the Fig. 7 (a), the bias pulse pumps the pseudospin in the positive $x$ direction since in this region $\psi_{xz}^2 > \psi_{yz}^2$, the pseudospin polarization of the tip points in the direction $-\hat{e}_x$ and the pseudospin accumulates in the opposite direction. In other terms, the orbital $L_{xz}$ will be mainly occupied. Vice versa, the blocking state has mainly a $L_{yz}$ component when the tip moves along the vertical arm of CuPc.
for the dynamics of the molecule. The block acting on
with any other state. Thus, the corresponding blocks are
just a slight shift in energy due to SOI but are not mixed
singlet states. The doublet and singlet states experience
number and can not split the time reversal symmetric
matrix discussed so far, since the SOI conserves particle

tation II is captured by an effective Hamiltonian, with the
initial thermal state, in which
configuration of the molecule remains much closer to the
nism cannot be visible within the 3 ps pulse time and the
Sizable oscillations in the y component of the pseudospin
(Fig. 7) show moreover that a linear superposition of both
orbitals is required to block the current. Almost no pseu-
dospin polarization is achieved along the horizontal and
vertical nodal planes, despite also here one of the two
orbitals dominates over the other. The tunnelling rate is
though so small that the interference blocking mecha-
ism cannot be visible within the 3 ps pulse time and the
configuration of the molecule remains much closer to the
initial thermal state, in which \( \langle \tau \rangle = 0 \).

\[ |T^0_\tau|, |T^{-1}_\tau|, |T^{-1}_\tau| \] it reads

\[
H_{\text{SOI}}^t = \begin{pmatrix}
\alpha_1/2 & 0 & 0 & 0 & \alpha_3 \\
0 & -\alpha_1/2 & 0 & 0 & \alpha_2 \\
0 & 0 & \alpha_4 & 0 & 0 \\
0 & 0 & 0 & \alpha_4 & 0 \\
\alpha_3 & 0 & 0 & 0 & \alpha_1/2
\end{pmatrix} + \alpha_5 \mathbb{1}_6. \tag{42}
\]

with \( \alpha_1 = 0.86 \text{ meV} \), \( \alpha_2 = 1.7 \times 10^{-2} \text{ meV} \), \( \alpha_3 = 8.27 \times 10^{-2} \text{ meV} \), \( \alpha_4 = 1.0 \times 10^{-2} \text{ meV} \) and \( \alpha_5 = -7.3 \times 10^{-2} \text{ meV} \).

The projection of \( H_{\text{SOI}}^t \) on the operator basis \( B^t \)

\[
H_{\text{SOI}} = (\alpha_4 + \alpha_5)\mathbb{1}_6 + \alpha_1 S_z \otimes \frac{\sigma_z}{2} - \alpha_4 S_{z^2} \otimes \mathbb{1}_2 \\
+ (\alpha_2 + \alpha_3)S_z \sigma_y \otimes \frac{\sigma_y}{2} + (\alpha_2 - \alpha_3)S_{xy} \otimes \frac{\sigma_y}{2}, \tag{43}
\]

highlights its ability to generate entangled evolution of
spin and pseudospin, due to the presence of several pro-
duct operator components which do not allow us to factor-
ize \( H_{\text{SOI}}^t \) as the tensor product of a spin and a pseudospin
operator. We show in Fig. 7 (c) and (d) the preparation
of the pseudospin in presence of the SOI. Qualitatively
we obtain the same texture of positive and negative ar-
areas for the \( x \) and \( y \) component of the SOI, but characte-
rized by an overall suppression of the absolute values.
To analyse this numerical result, we refer once
more to the equation of motion for expectation value of
the pseudospin.

The only component of the \( H_{\text{SOI}} \) able to generate an
appreciable pseudospin dynamics during the 3 ps time
lapse of the bias pulse considered so far is the one pro-
portional to \( \alpha_1 \). The latter reads \( \alpha_1 S_z \otimes \frac{\sigma_z}{2} \) and is factor-
ized into the tensor product of a spin and a pseudospin
operator. It is thus convenient to study the dynamics of
the correlators

\[
\langle \tau^\pm \rangle := \text{Tr} \left\{ \rho^t \left[ \frac{1}{3} \mathbb{1}_3 + \frac{1}{6} S_z \pm \frac{\sigma_z}{2} \right] \otimes \frac{\sigma_y}{2} \right\},
\]

\[
\langle \tau^0 \rangle := \text{Tr} \left\{ \rho^t \left[ \frac{1}{3} (\mathbb{1}_3 - S_z) \otimes \frac{\sigma_y}{2} \right] \right\}, \tag{44}
\]

which are the projections of the pseudospin operator on
the subspaces with spin component \( S_z = \pm 1 \) and \( S_z = 0 \),
respectively. Their equations of motion follow from the
generalized master equation \( \dot{\rho} = (\mathcal{L}_M + \mathcal{L}_T)\rho \)
approximated to retain only the contribution of the SOI Ham-
ltonian generating the fastest dynamics

\[
\frac{d}{dt} \langle \tau^\pm \rangle = - \sum_{\eta} \Gamma_{\eta} f^- \langle \epsilon_\eta \rangle \langle \tau^\pm \rangle \pm \frac{\alpha_1}{\hbar} \epsilon_z \times \langle \tau^\pm \rangle \\
+ \Gamma_{\text{tip}} \left( \frac{1}{2} f_{\text{tip}} (\epsilon_t) \rho^d - \frac{1}{2} f_{\text{tip}} (\epsilon_t) \rho^\pm \right) P_\tau, \tag{45}
\]

\[
\frac{d}{dt} \langle \tau^0 \rangle = - \sum_{\eta} \Gamma_{\eta} f^- \langle \epsilon_\eta \rangle \langle \tau^0 \rangle \\
+ \Gamma_{\text{tip}} \left( \frac{1}{2} f_{\text{tip}} (\epsilon_t) \rho^d - \frac{1}{2} f_{\text{tip}} (\epsilon_t) \rho^0 \right) P_\tau,
\]

B. Influence of the spin orbit interaction

The effect of the SOI on the spectrum analyzed in Sec-
tion II is captured by an effective Hamiltonian, with the
same block diagonal structure as the one of the density
matrix discussed so far, since the SOI conserves particle
number and can not split the time reversal symmetric
singlet states. The doublet and singlet states experience
just a slight shift in energy due to SOI but are not mixed
with any other state. Thus, the corresponding blocks are
proportional to the identity matrix and not of interest
for the dynamics of the molecule. The block acting on
the triplet states is the most interesting part of the SOI
effective Hamiltonian. In the basis \( |T^1_\tau \rangle, |T^{-1}_\tau \rangle, |T^{-1}_\tau \rangle \),
coupling limit, we neglect the SOI and only different degenerate energy levels. Due to the singular numerator on the (degenerate) energy level with particle number $N$ and energy $E$, the collective index $m$ labels the different degenerate energy levels. Due to the singular coupling limit, we neglect the SOI and only $H_0$ is taken into account in the calculation of $H_{LS}$. The logarithmic tails of the digamma function, force us to keep the entire spectrum of both neighbouring particle numbers into account. We thus avoid convergence problems in the calculation of $H_{LS}$. For the case at hand the contri-

\[ H_{LS} = -\frac{1}{2\pi} \sum_{NE\eta} \sum_{i,j,\sigma} \Gamma^{\eta}_{i,j,\sigma} \mathcal{P}^{NE} \left[ d_{i\sigma}^\dagger p_\eta (E - H_0) d_{j\sigma} + d_{j\sigma} p_\eta (H_0 - E) d_{i\sigma}^\dagger \right] \mathcal{P}^{NE}, \]

where $\mathcal{P}^{NE} = \sum_m \langle NEm | NEm \rangle$ is the projection operator on the (degenerate) energy level with particle number $N$ and energy $E$. The collective index $m$ labels the different degenerate energy levels. Due to the singular coupling limit, we neglect the SOI and only $H_0$ is taken into account in the calculation of $H_{LS}$. The logarithmic tails of the digamma function, force us to keep the entire spectrum of both neighbouring particle numbers into account. We thus avoid convergence problems in the calculation of $H_{LS}$. For the case at hand the contri-
butions of the high energy neutral states compensate, in fact, the ones of the high energy doubly charged molecule (CuPc$^{2^-}$).

In Fig. 9(a) we show the state of the molecule obtained after the pump pulse taking into account the Lamb shift corrections. The Lamb shift correction is responsible of a $\langle \tau_z \rangle$ of the order of $10^{-3}$. In comparison, $\langle \tau_z \rangle$ is negligible, if we only consider the tunnelling dynamics and the SOI. Despite its modest effects in the pulsed dynamics, the non-zero $\langle \tau_z \rangle$ component obtained here is amplified by the SOI during the free evolution following the pulse (see Fig. 10). Moreover, the presence of an imbalance in the occupation of opposite angular momentum states opens the question about circular currents triggered by the coupling to the leads and their feedback on the electronic structure of the molecule [61].

The results presented in Fig. 9 (a) can be understood by analyzing the structure of the Lamb shift Hamiltonian. The latter is block diagonal in the doublet, triplets and singlets subspaces and spin isotropic. By neglecting the components proportional to the identity, which drop by analyzing the structure of the Lamb shift Hamiltonian (see Fig. 10). Moreover, the presence of an imbalance in the occupation of opposite angular momentum states opens the question about circular currents triggered by the coupling to the leads and their feedback on the electronic structure of the molecule [61].

The results presented in Fig. 9 (a) can be understood by analyzing the structure of the Lamb shift Hamiltonian. The latter is block diagonal in the doublet, triplets and singlets subspaces and spin isotropic. By neglecting the components proportional to the identity, which drop from $\mathcal{L}_{LS}$, we can write the general form for the singlets and triplet blocks, respectively

$$H_{LS}^t = \hbar \omega_{LS}^t \cdot \frac{\sigma}{2},$$
$$H_{LS}^s = \mathbb{1}_3 \otimes \hbar \omega_{LS}^s \cdot \frac{\sigma}{2},$$

from which it is clear that the Lamb shift Hamiltonian acts on the singlet as well as on the triplet subspace as a pseudo magnetic field. The latter adds, during the short pump pulse, to the spin dependent pseudo magnetic field associated to the SOI which was introduced in Eq. (45). The strength and the direction of the pseudo-magnetic fields $\omega_{LS}^s$ and $\omega_{LS}^t$ are obtained from the direct evaluation of Eq. (46) for the anionic subspace of CuPc. By following the derivation in [47] adapted to the $D_{4h}$ point group symmetry of the CuPc [62], we get

$$\omega_{LS}^{s/t} = \Gamma_{tip} (A^{s/t} P_\tau + B^{s/t} Q_\tau),$$

where

$$Q_\tau = \frac{1}{\psi_{xz}^2 + \psi_{yz}^2} \begin{pmatrix} \psi_{xz}^2 - \psi_{yz}^2 \\ -2\psi_{xz}\psi_{yz} \\ 0 \end{pmatrix},$$

while $A^{s/t}$ and $B^{s/t}$ are real numbers which depend on the electronic structure of the molecule and on the applied bias across the junction. Specifically, they read respectively for the triplet and for the singlet

$$A^t = -\frac{1}{6\pi} \sum_{S_{i}\sigma} \left[ (T_{+}^{S_{i}}) d_{L+,\sigma}^{s} P_{T}(E^{t} - H_{0}) d_{L-,\sigma}^{s} \right] T_{+}^{S_{i}},$$
$$B^t = -\frac{1}{6\pi} \sum_{S_{i}\sigma} \left[ (T_{-}^{S_{i}}) d_{L-,\sigma}^{s} P_{T}(E^{t} - H_{0}) d_{L+,\sigma}^{s} \right] T_{-}^{S_{i}},$$

and

$$A^s = -\frac{1}{2\pi} \sum_{\sigma} \left[ (S_{+}^{s}) d_{L+,\sigma}^{s} P_{T}(E^{s} - H_{0}) d_{L-,\sigma}^{s} \right] S_{-},$$
$$B^s = -\frac{1}{2\pi} \sum_{\sigma} \left[ (S_{-}^{s}) d_{L-,\sigma}^{s} P_{T}(E^{s} - H_{0}) d_{L+,\sigma}^{s} \right] S_{+}.$$}

The pseudo magnetic fields acting on the triplet and singlet subspaces differ, in general, in strength and direction. In order to achieve a qualitative understanding of the results in Fig. 9 it is useful to concentrate on their dependence on the tip position, expressed through the vectors $P_\tau$ and $Q_\tau$. Given that the tunnelling pumps the pseudospin along the direction $-P_\tau$, the direction and frequency of the precession induced by $H_{LS}$ at a given bias is readily obtained by the vector product

$$\omega_{LS}^{s/t} \times P_\tau = -2B^{s/t} \frac{\psi_{xz}}{\gamma_{0} \psi_{xz}} \frac{\psi_{xz}^2 - \psi_{yz}^2}{\psi_{xz}^2 + \psi_{yz}^2},$$

which is proportional to the torque acting on the pseudospin when the latter is pumped in the direction of the dark state. Since the time lapse of the pump pulse is
less than a quarter of the precession period induced by the Lamb shift, the direction and intensity of the torque are proportional to the ones of the \( z \) component of the pseudospin just after the pulse. In Fig. 9 we see a comparison between the simulated \( z \) component of the pseudospin and the torque, normalized to its maximum value, as obtained from Eq. (52). The torque vanishes when \( P r \) is parallel or antiparallel to \( Q r \). For this reason we see no \( z \) component of the pseudospin along the \( x \) and \( y \) axis where either one or the other LUMO orbital vanishes and along the diagonals \( x_{\text{tip}} = \pm y_{\text{tip}} \) where the two orbitals necessarily assume the same absolute value. Moreover, the torque is strongly suppressed on the outer parts of the ligand arms where one of the two real valued LUMOs has much more weight than the other one. Finally, as can be readily checked from the Eq. (52), the pattern of \( \langle \tau_z \rangle \) obtained from the pump pulse is invariant under rotations of \( \pi/2 \) around the main rotational axis and anti-symmetric with respect to the four vertical symmetry planes of CuPc. From these properties it derives a certain resemblance to the HOMO of the molecule.

IV. FREE EVOLUTION AND READ OUT

The intricate dynamics triggered by the pump pulse brings the CuPc molecule from its thermal equilibrium into an excited, coherent superposition of many-body states. The latter, as we have shown, can be controlled by the tip position and the duration of the pump pulse. We focus, in this section, on the following time lapse in which the free evolution in absence of bias reveals an intertwined spin and pseudospin dynamics. Moreover we introduce a second pulse to achieve a stroboscopic readout and investigate the evolution of the molecule during the delay time between the pump and the probe pulse.

A. Free evolution

The state prepared by the pump pulse is a superposition of several anionic states. Once the external bias turns back to zero, tunnelling events are strongly suppressed due to the large charging energy of the molecule with respect to temperature and the charge is conserved. The time evolution is described only by the singlet and triplet subblocks of the reduced density matrix. Moreover, there is no coupling between the singlet and the triplet state, which thus evolve independently, as an incoherent superposition. Specifically, as the singlet energy eigenstates are connected by time reversal symmetry, they are degenerate and thus they show no dynamics at all. In contrary, the triplet state is characterized by an intertwined spin and pseudospin dynamics, due to the SOI, and by the pseudospin precession due to the Lamb shift, as described in the previous section.

In Fig. 10 we present the time evolution of the three components of the pseudospin during 100 ps, starting from the beginning of the pump pulse. In Fig. 10 (a) we first concentrate, for simplicity, on the evolution generated solely by the SOI-Hamiltonian (the contribution of \( H_0 \) drops from the Liouvillian, being just a uniform energy shift). The \( x \) and \( y \) components show beating dynamics with the fast oscillations compatible with the largest SOI induced splitting \( \alpha_1 \) and the slow modulation associated to the smaller energy separations \( \alpha_2 \) and \( \alpha_3 \) between the two triplet states with the lowest and, respectively, the highest energies. As we already discussed in the previous section, the \( z \) component of the pseudospin is conserved by the part of \( H_{\text{SOI}} \) proportional to \( \alpha_1 \) and thus it can only exhibit slow dynamics.

Further insight into the free evolution is given by the analytic result plotted as dashed black line in Fig. 10. We obtain it by solving the coherent contribution of the GME \( \dot{\rho} = -\frac{i}{\hbar} [H_{\text{SOI}}, \rho] \), projected into the operator basis introduced in Section II D. The \( x \) component of the
pseudospin evolves as
\[
\langle \tau_z \rangle(t) = \langle \tau_z \rangle_0 + \frac{1}{3} \left( \langle \tau_z \rangle_0 - \langle S_z^x \tau_z^t \rangle_0 \right) + \\
\frac{1}{12} \left[ \sqrt{a^2 + c^2} \cos \left( \omega_1 t + \arctan \left( \frac{c}{a} \right) \right) + \right. \\
\left. \sqrt{b^2 + d^2} \cos \left( \omega_2 t + \arctan \left( \frac{d}{b} \right) \right) \right],
\]  
(53)
where the two oscillation frequencies are
\[
\omega_1 = \frac{1}{\hbar} (\alpha_1 + \alpha_2 - \alpha_3) \quad \text{and} \quad \omega_2 = \frac{1}{\hbar} (\alpha_1 - \alpha_2 + \alpha_3),
\]  
(54)
while the amplitudes and phases are expressed in terms of the four coefficients
\[
a = 4\langle \tau^t_z \rangle_0 + 2\langle S^y_z \tau^t_x \rangle_0 - 3\langle S^x_z \tau^t_y \rangle_0,
\]  
b = 4\langle \tau^t_y \rangle_0 + 2\langle S^z_x \tau^t_z \rangle_0 + 3\langle S^x_z \tau^t_y \rangle_0,
\]  
c = 6\langle S^z_x \tau^t_y \rangle_0 - \langle S^y_z \tau^t_z \rangle_0,
\]  
d = 6\langle S^z_x \tau^t_y \rangle_0 + \langle S^y_z \tau^t_z \rangle_0,
\]  
(55)
which contain several triplet correlators calculated at the time \( t = 0 \) at which the pump pulse terminates. In the first line in Eq. (53) one recognizes the constant terms associated to the singlet and the \( S_z = 0 \) component of the pseudospin. The second and the third line, instead, describe the dynamics of the \( S_z = \pm 1 \) components intertwined by the SOI. The close frequencies \( \omega_1 \) and \( \omega_2 \) are at the origin of the beatings observed in Fig. 10. Moreover, it is clear that the pseudospin at time \( t > 0 \) depends on several mixed correlators, e.g. \( \langle S^x_z \tau^t_y \rangle_0 \) calculated at initial time, thus revealing the interplay of spin and pseudospin in the evolution of CuPc.

The analogous expressions for the time evolution of the \( y \) and \( z \) components of the pseudospin can be found in the Appendix B. Here we just mention that the \( y \) component combines oscillations with frequencies \( \omega_3 = (\alpha_1 - \alpha_2 - \alpha_3)/\hbar \) and \( \omega_4 = (\alpha_1 + \alpha_2 + \alpha_3)/\hbar \), thus featuring also beating dynamics, while the \( z \) component contains only the smaller frequencies \( \alpha_2/\hbar \) and \( \alpha_3/\hbar \). In summary, all possible Bohr frequencies associated to the two lowest and two highest triplet states are reflected into the dynamics of the pseudospin.

The spin and orbital correlation is further demonstrated by the comparison of the mixed triplet correlators with the product of the single expectation values. As shown in Fig. 11 the mixed correlators are essentially equal to their factorized counterpart at \( t = 0 \) when the reduced density matrix is in thermal equilibrium. The situation changes drastically during the pump pulse and remains essentially the same during the free evolution, thus demonstrating the correlation between the two degrees of freedom of the molecule.

Eventually, we show in Fig. 10 (b) the combined effects of the SOI and the Lamb shift correction on the evolution of the CuPc anionic state. The combination of the effective magnetic fields associated to the SOI and to the Lamb shift correction, the first oriented along the \( z \) axis, the second in the \( xy \) plane, mixes the time evolution of the different pseudospin components. The result is a more complex, but also more homogeneous oscillation beating pattern, now visible in all three components.

### B. Transferred charge

In this section we propose a readout mechanism for the observation of the SOI induced dynamics described so far. To this end we simulate a short (0.5 ps) overthreshold probe pulse following the pump pulse at a variable delay time. The observable is the total charge transferred through the molecule and collected into the tip, calculated as a function of the delay time.

In Fig. 12 we show the result of our simulations, with the charge transferred to the tip per pump probe cycle in units of the electronic elementary charge. Despite the sequential tunnelling regime, fractional charge can be transferred through the molecule. The result should be interpreted in a probabilistic sense, with the charge averaged over a great number of pump probe cycles. The high frequency repetition of the pump probe pulse is anyway necessary in the experiments, with the aim to obtain a measurable average current, i.e. the mean transferred charge per pump probe cycle divided by the repetition period \([2, 3]\). It is crucial, though, for the meaningful comparison of the experimental data with the theoretical predictions presented here that the repetition period is longer than the relaxation time of the molecule towards its thermal equilibrium. The latter is in fact assumed as the starting point of the excitations induced by the pump pulse.

The beatings in the transferred charge per cycle presented in Fig. 12 closely resemble the ones obtained in the free evolution of the pseudospin shown in Fig. 10 (b), thus indicating that the proposed measurement of the
transferred charge can give information about the SOI induced dynamics on the system.

This similarity can be rationalized starting from the following observations. The dynamics induced on the junction by the probe pulse closely resembles the one produced by the pump pulse, with the bias across the junction allowing energetically the transition between the anionic and the neutral states of the molecule. There are though two crucial differences. Firstly, the probe pulse impinges on the molecule when the latter is far from equilibrium: it is instead characterized by a significant population of the singlet states, a finite pseudospin, an anisotropic spin state and it even shows correlations between the spin and the pseudospin degrees of freedom, as we demonstrated in the previous sections. Secondly, due to its much shorter duration, the probe pulse is not capable to induce a significant variation of the pseudospin on the system, though it is long enough to ensure, in principle, a measurable charge transfer to the tip.

Crucially, the probability for charge transfer to occur during the probe pulse depends on the state of CuPc at the beginning of the pulse. The closer is the molecular state to the electronic dark state (see the condition given in Eq. (41)), the less probable is the tunnelling event which brings an electron from the molecule towards the tip. As the pseudospin dynamics during the delay time between the pump and the probe pulses is strongly influenced by the SOI, the latter leaves its clear fingerprints also in the average transferred charge.

In first approximation, we can formalize the ideas just expressed in the following equation for the transferred charge

\[ q_{\text{tr}}(t) = q_0 + \Gamma_{\text{tr}} \delta t \left[ 1 + 2 \langle \tau \rangle(t) \cdot \mathbf{P}_z \right], \tag{56} \]

where \( q_0 \) is the charge transferred during the pump pulse, \( \delta t \) is the length of the probe pulse and \( \langle \tau \rangle(t) \) is the pseudospin of the molecule at the beginning of the probe pulse. This result is derived from the formal expression for the current given in Eq. (25) under the approximation that, during the probe pulse, neither the jump operators nor the reduced density matrix for the system depend on time and in the high bias limit in which unidirectional transport is enforced.

In Fig. 12 we show a comparison between the numerical calculation of the transferred charge and its evaluation based on Eq. (56). Despite of the rather crude approximations present in its derivation, Eq. (56) captures essentially all the features in the dynamics of the transferred charge. The systematical slight overshoot of the analytical evaluation can most probably be attributed to tendency of the probe pulse to orient the pseudospin towards the dark state direction, neglected in the derivation of Eq. (56).

All the information about the SOI induced dynamics is included in Eq. (56) through the pseudospin \( \langle \tau \rangle(t) \) calculated at the delay time \( t \). Indeed, as we have already discussed, the pseudospin beatings contain all Bohr frequencies of the triplet low energy states. Thus, monitoring the dynamics of the transferred charge gives access to the SOI induced spectrum. Moreover, an interesting aspect of the molecular many-body state can be observed, since we can also read out the projection of the pseudospin along the known direction \( P_z \).

Eventually, we expect the transferred charge to be also strongly dependent on the tip position. On the one hand, the overall constant shift \( q_0 \) depends on the position as well as the average tip rate which is proportional to \( \psi_{g_2}^{+}(r_{\text{tip}}) + \psi_{g_2}^{2}(r_{\text{tip}}) \). Moreover, the tip position influence the prepared pseudospin since both the dark state as well as the torque induced by the Lamb shift show characteristic pattern. The tip position can even modulate the very dynamics of the pseudospin via the pseudomagnetic fields \( \omega_{LS}^{z} \). The analysis of these effects, though, goes beyond the scope of this work.

V. CONCLUSIONS

The theoretical investigation of a lightwave-STM single molecule junction is on the focus of this manuscript. In particular, we studied how to access, via a stroboscopic pump probe scheme, the spin orbit induced electronic dynamics of a copper phthalocyanine. To this end, we extended the transport theory for STM on thin insulating films [47] to include the effects of laser pulses, specific of a lightwave-STM, directly in the time domain. We identify in the coherent superposition of different angular momentum states the fundamental mechanism for the triggering and read out of spin orbit induced dynamics. The method of choice is a generalized master equation (GME) for the reduced density matrix, which allows for the treatment of strong correlation on the CuPc weakly coupled to both the substrate and the tip. The tunnelling and the SOI induced dynamics share similar time scales resulting in a non adiabatic time evolution of the system.

The localized tunnelling at the tip combined with the quasi-degenerate spectrum of the molecule allows for interference effects to appear. The pump pulse takes the
molecule out of its thermal equilibrium and brings it towards an electronic dark state, associated to a specific pseudospin configuration, i.e. a coherent superposition of angular momentum states. After the lightwave induced bias is turned off again, the system shows an intricate beating dynamics of the pseudospin. The latter is driven at the same time by the spin orbit interaction and by virtual electronic fluctuations between the molecule and the tip (the Lamb shift). In particular, oscillations at all the Bohr frequencies associated to the spectrum of $H_{SOI}$ contribute to the time evolution of the pseudospin.

Further, we propose to use a second, shorter, bias pulse in order to probe the many-body state acquired by the system after a given delay time separating the two pulses. Specifically, the charge transferred during the probe pulse is proportional to the projection of the pseudospin along the known dark state direction. Ultimately, monitoring the beatings in the average charge per pump probe cycle allows one to access the spin orbit induced dynamics of a CuPc.

Both the electronic dark state as well as the pseudospin torque induced by the Lamb shift vary with the tip position with patterns obtained by different combinations of the LUMO wave functions, as can be seen by comparing Figs. 7 and 9 with Eqs. (38) and (52). We expect those patterns to leave their signatures in the pseudospin dynamics and ultimately to emerge in the transferred charged recorded as a function of tip position and time. The high temporal and spatial resolution demonstrated in lightwave-STM experiments [2, 3] is certainly capable to detect those patterns.

Moreover we expect the theoretical method presented in this manuscript to open new paths for the investigation on the electronic dynamics with lightwave-STM. Exemplarily, ferromagnetic leads, besides working as sources of polarized electrons, can induce proximity effects in single molecule junctions. Dipolar (and also quadrupolar for systems with high spin, $S > \frac{1}{2}$) exchange fields arise which influence the electronic dynamics on the molecule and its transport characteristics. Such proximity effects could be simultaneously controlled and monitored in a spin polarized lightwave-STM. Moreover, the interplay with mechanical degrees of freedom could be investigated directly in the time domain, thus revealing new aspects of the spin-orbit induced dynamics in single molecules.

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Appendix A: Quasi-stationary high bias limit

The tunneling Liouvillian written in the basis Eq. (A1) has the following form

$$\mathcal{L}_{tun} = \begin{pmatrix}
\mathcal{L}_D^{\dagger} & \mathcal{L}_D^{\dagger} & \mathcal{L}_D & \mathcal{L}_D & \mathcal{L}_D
\end{pmatrix}
\begin{pmatrix}
0 & 0 & 0 & 0 & 0
0 & 0 & 0 & 0 & 0
0 & 0 & 0 & 0 & 0
0 & 0 & 0 & 0 & 0
0 & 0 & 0 & 0 & 0
\end{pmatrix}
\begin{pmatrix}
\mathcal{L}_D & \mathcal{L}_D & \mathcal{L}_D & \mathcal{L}_D & \mathcal{L}_D
\end{pmatrix}
$$

(A2)

Explicitly, we have the term describing the depopulation of the doublet states towards the anionic states

$$\mathcal{L}_D^{\dagger} = \mathcal{L}_D^{\dagger} = -\Gamma sub(3f^{\dagger}_{sub}(\epsilon_t) + f^{\dagger}_{sub}(\epsilon_s))$$

(A3)

with $\epsilon_t$, $\epsilon_s$ introduced in Eq. (37).

The depopulation of the anionic states are $2 \times 2$ matrices which read for the triplets

$$\mathcal{L}_{T^{+1}} = \mathcal{L}_{T^{0}} = \mathcal{L}_{T^{-1}} = \begin{pmatrix}
-\Gamma sub f^{\dagger}_{sub}(\epsilon_t) - \Gamma tip f^{\dagger}_{tip}(\epsilon_t) & 0 \\
0 & -\Gamma sub f^{\dagger}_{sub}(\epsilon_t)
\end{pmatrix},$$

(A4)

and for the singlets

$$\mathcal{L}_{SS} = \begin{pmatrix}
-\Gamma sub f^{\dagger}_{sub}(\epsilon_s) - \Gamma tip f^{\dagger}_{tip}(\epsilon_s) & 0 \\
0 & -\Gamma sub f^{\dagger}_{sub}(\epsilon_s)
\end{pmatrix}.$$  

(A5)

The tunneling from the $|T^{-1}\rangle$ states to $|D^{\dagger}\rangle$ is the same as from $|T^{-1}\rangle$ to $|D^{\dagger}\rangle$

$$\mathcal{L}_D^{\dagger} = \mathcal{L}_D^{\dagger} = \begin{pmatrix}
\Gamma sub f^{\dagger}_{sub}(\epsilon_t) + 2\Gamma tip f^{\dagger}_{tip}(\epsilon_t), & \Gamma sub f^{\dagger}_{sub}(\epsilon_t)
\end{pmatrix},$$

(A6)
whereas tunneling from the $|T^0\rangle$ states is possible to both doublet states but every channel has a smaller "effective" rate

$$\mathcal{L}_{D^+T^0} = \mathcal{L}_{D^+T^0} = \left(\frac{\Gamma_{\text{sub}}}{2} f_{\text{sub}}^-(\epsilon_1) + \Gamma_{\text{tip}} f_{\text{tip}}^-(\epsilon_1), \frac{\Gamma_{\text{sub}}}{2} f_{\text{sub}}^-(\epsilon_1)\right). \quad (A7)$$

The same holds true for the singlets

$$\mathcal{L}_{D^+S} = \mathcal{L}_{D^+S} = \left(\frac{\Gamma_{\text{sub}}}{2} f_{\text{sub}}^-(\epsilon_s) + \Gamma_{\text{tip}} f_{\text{tip}}^-(\epsilon_s), \frac{\Gamma_{\text{sub}}}{2} f_{\text{sub}}^-(\epsilon_s)\right). \quad (A8)$$

The re-population rates of the $|T^{+1}\rangle$ and $|T^{-1}\rangle$ states are given by

$$\mathcal{L}_{T^{+1}D^+} = \mathcal{L}_{T^{-1}D^+} = \left(\Gamma_{\text{sub}} f_{\text{sub}}^+(\epsilon_1) + \Gamma_{\text{tip}} f_{\text{tip}}^+(\epsilon_1), \frac{\Gamma_{\text{sub}}}{2} f_{\text{sub}}^+(\epsilon_1)\right)^\dagger. \quad (A9)$$

Furthermore, we have the re-population of the $|T^0\rangle$ states

$$\mathcal{L}_{T^0D^+} = \mathcal{L}_{T^0D^+} = \left(\Gamma_{\text{sub}} f_{\text{sub}}^+(\epsilon_1) + \Gamma_{\text{tip}} f_{\text{tip}}^+(\epsilon_1), \frac{\Gamma_{\text{sub}}}{2} f_{\text{sub}}^+(\epsilon_1)\right)^\dagger, \quad (A10)$$

and the singlets

$$\mathcal{L}_{SD^+} = \mathcal{L}_{SD^+} = \left(\Gamma_{\text{sub}} f_{\text{sub}}^+(\epsilon_s) + \Gamma_{\text{tip}} f_{\text{tip}}^+(\epsilon_s), \frac{\Gamma_{\text{sub}}}{2} f_{\text{sub}}^+(\epsilon_s)\right)^\dagger. \quad (A11)$$

By solving the eigenvalue equation

$$\mathcal{L}_T \rho_i = \Gamma_i \rho_i, \quad (A12)$$

we associate a tunneling rate $\Gamma_i$ to an eigenstate of the tunneling Liouvillian $\rho_i$. The $\rho_i$ form a basis and therefore we can expand the thermal density matrix in this basis as

$$\rho_{\text{thermal}} = \sum_i A_i^0 \rho_i, \quad (A13)$$

with expansion coefficients $A_i^0$. The time evolution of a density matrix is governed by

$$\dot{\rho} = \mathcal{L}_T \rho, \quad (A14)$$

which has the solution

$$\rho(t) = e^{\mathcal{L}_T t} \rho_{\text{thermal}} = \sum_i A_i^0 e^{-\Gamma_i t} \rho_i. \quad (A15)$$

We find for the rates $\Gamma_i$ five different energy scales

\begin{align*}
\hbar \Gamma_{1/2} & \sim \text{meV}, & \hbar \Gamma_{3-6} & \sim 10^{-1} \text{ meV}, \\
\hbar \Gamma_7 & \sim 10^{-35} \text{ meV}, & \hbar \Gamma_{8/9} & \sim 10^{-38} \text{ meV}, \quad (A16) \\
\hbar \Gamma_{10} & = 0 \text{ meV}.
\end{align*}

The eigenvectors $\rho_i$ with $i = 1 - 6$ thus do not contribute to the density matrix on the timescale set by the pump laser pulse. The state $\rho_{10}$ represents the steady state solution of the master equation given by the thermal distribution of the populations of the coupled singlet and triplet states. The three remaining eigenstates $\rho_{7-9}$ do not decay on the time scales of our simulations. The depopulating rate of a singlet state via a substrate tunnelling transition sets the order of magnitude of $\Gamma_7 \sim \Gamma_{\text{sub}} f_{\text{sub}}^-(\epsilon_1)$, whereas $\Gamma_{8/9} \sim \Gamma_{\text{sub}} f_{\text{sub}}^-(\epsilon_1)$ are of the order of the substrate depopulating rate of a triplet state.

### Appendix B: Free evolution of the pseudospin components $\langle \tau_y \rangle$ and $\langle \tau_z \rangle$

We give here the analytical expression of the time evolution of the $y$ and $z$ components of the pseudospin solely under the influence of $H_{\text{SOI}}$. The $y$ component reads

$$\langle \tau_y(t) \rangle = \frac{1}{3} \left( \langle \tau_y^4 \rangle_0 - \langle S_x^4 \tau_{y}^{4} \rangle_0 \right) + \langle \tau_y^4 \rangle_0 + \frac{1}{12} \sqrt{a_y^2 + c_y^2} \cos \left( \omega_y t - \arctan \frac{c_y}{a_y} \right) + \frac{1}{12} \sqrt{b_y^2 + d_y^2} \cos \left( \omega_y t - \arctan \frac{d_y}{b_y} \right), \quad (B1)$$

where the two frequencies are given by

$$\omega_3 = \frac{1}{\hbar} (\alpha_1 - \alpha_2 - \alpha_3) \quad \text{and} \quad \omega_4 = \frac{1}{\hbar} (\alpha_1 + \alpha_2 + \alpha_3). \quad (B2)$$

The phases and amplitudes of the oscillations are obtained from the four parameters

\begin{align*}
a_y & = 4 \langle \tau_y^4 \rangle_0 + 3 \langle S_x^4 \tau_y^4 \rangle_0 + 2 \langle S_z^4 \tau_y^4 \rangle_0, \\
b_y & = 4 \langle \tau_y^4 \rangle_0 - 3 \langle S_x^4 \tau_y^4 \rangle_0 + 2 \langle S_z^4 \tau_y^4 \rangle_0, \\
c_y & = 6 \langle S_x^4 \tau_y^4 \rangle_0 + 2 \langle S_z^4 \tau_y^4 \rangle_0, \\
d_y & = 6 \langle S_x^4 \tau_y^4 \rangle_0 - 2 \langle S_z^4 \tau_y^4 \rangle_0, \quad (B3)
\end{align*}

which can be calculated from the several expectation values and correlators calculated at the initial time $t = 0$. The $z$ component does only exhibit slower dynamics and is described by

$$\langle \tau_z(t) \rangle = \frac{1}{3} \left( \langle \tau_z^4 \rangle_0 - \langle S_x^4 \tau_z^4 \rangle_0 \right) + \langle \tau_z^4 \rangle_0 + \frac{1}{12} \sqrt{a_z^2 + c_z^2} \cos \left( \frac{\alpha_z}{\hbar} t - \arctan \frac{c_z}{a_z} \right) + \frac{1}{12} \sqrt{b_z^2 + d_z^2} \cos \left( \frac{\alpha_z}{\hbar} t - \arctan \frac{d_z}{b_z} \right), \quad (B4)$$

with

\begin{align*}
a_z & = 4 \langle \tau_z^4 \rangle_0 - 3 \langle S_x^4 \tau_z^4 \rangle_0 + 2 \langle S_z^4 \tau_z^4 \rangle_0, \\
b_z & = 4 \langle \tau_z^4 \rangle_0 + 3 \langle S_x^4 \tau_z^4 \rangle_0 + 2 \langle S_z^4 \tau_z^4 \rangle_0, \\
c_z & = 3 \langle S_x^4 \tau_z^4 \rangle_0 - \langle S_z^4 \tau_z^4 \rangle_0, \\
d_z & = 3 \langle S_x^4 \tau_z^4 \rangle_0 + \langle S_z^4 \tau_z^4 \rangle_0. \quad (B5)
\end{align*}
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