

14 Electronic Transport in Correlated Single-Molecule Junctions

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1 Introduction

The nanometer size, the perfect reproducibility and, at the same time, the huge variety of chemical compounds make molecular electronics an attractive bottom up approach to the quest of circuit miniaturization [1, 2]. A single-molecule junction (SMJ) is the archetypal device: ideally it only consists of a molecule contacted to metallic electrodes. Despite their deceptive simplicity, such devices explore a whole range of complex phenomena. Their electronic transport characteristics carry the fingerprints of the contacted molecule, primarily its correlated electronic structure, but also its mechanical excitations, spin dynamics, the response to external stimuli, as illumination, electrostatic gating, mechanical stress, or temperature gradient [3].

Here we will concentrate on the signatures of electronic correlation. Firstly, we can classify the effects of electronic correlation in extrinsic and intrinsic. Both of them stem from the interplay of electron-electron interaction on the molecule and the coupling to the electrodes. Extrinsic effects, though, (e.g. the Kondo [4–6], Yu-Shiba-Rusinov resonances [6–8], and many-body interference [9–12]) rely, for their appearance, on a specific property of the lead or of its coupling to the molecule. Intrinsic correlation phenomena, instead, arise directly from the entangled nature of the molecular eigenstates. The coupling to the leads is here only a tool to probe the electronic correlation and translate it into a specific transport signal. Examples of such effects are the excitonic dynamics [13], the equilibrium and non-equilibrium spin crossover [14–17], the magnetic anisotropy in single-molecule magnets [18–20], the charge dependent tunneling barrier modification [21] or the apparent orbital inversion discussed below [22]. Intrinsic correlation effects can only be captured within a many-body description of the molecular electronic structure. The latter is theoretically understood, in absence of major structural relaxations, as the complete set of eigenstates and eigenvalues of the Hamiltonian

$$\hat{H}_{\text{mol}} = \sum_i \varepsilon_i \hat{n}_i + \frac{1}{2} \sum_{ijkl} \sum_{\sigma\sigma'} V_{ijkl} \hat{d}_{i\sigma}^\dagger \hat{d}_{j\sigma'}^\dagger \hat{d}_{k\sigma} \hat{d}_{l\sigma}, \quad (1)$$

where the first term includes the (single particle) molecular orbital energies ε_i with the correspondent occupation operator $\hat{n}_i$ and the second describes the electron-electron interaction among the electrons. In its elementary form, the state of the molecule is given by the occupation of molecular orbitals according to the Pauli exclusion principle, thus neglecting electron-electron interaction. In the ground state all levels up to the highest occupied molecular level (HOMO) are filled, leaving empty the higher energy ones starting with the lowest unoccupied molecular level (LUMO). Transitions from an occupied to an empty level, or the addition (removal) of electrons, account for all electronic excitations. Such a description neglects correlations and assumes the electrons to be independent, thus giving many-body wave functions in the form of single Slater determinants. The simplest model able to describe the extrinsic correlated transport phenomena is the Anderson impurity model, in which the impurity Hamiltonian is of the form of Eq. (1) with a single orbital and the four associated eigenstates are the uncorrelated single Slater determinants

$$|0\rangle = |\emptyset\rangle, \quad |\uparrow\rangle = \hat{d}_\uparrow^\dagger |\emptyset\rangle, \quad |\downarrow\rangle = \hat{d}_\downarrow^\dagger |\emptyset\rangle, \quad |2\rangle = \hat{d}_\uparrow^\dagger \hat{d}_\downarrow^\dagger |\emptyset\rangle.$$

For more complex systems with a finite spatial extension different approximation schemes can be applied. In general, the long range, slow varying contribution of the Coulomb interaction can be incorporated within a mean-field approach, giving rise to occupation dependent shifts in the orbital energies and changes in the orbital shapes (orbital mixing). The short range, rapidly decaying contribution is instead responsible for exchange and correlation effects which can only be captured within a multi Slater-determinant description. A strong coupling to the metallic electrodes typically justifies (due to the hybridization and efficient metallic screening) a single-particle approach with independent electrons and mean field treatment. In the weak-coupling regime, electronic correlations become relevant as soon as the single-particle level splitting $\varepsilon_i - \varepsilon_j$ is comparable to the exchange V_{ijij} or pair hopping V_{iijj} energies. The discussion of intrinsic correlation phenomena arising in this regime is the main focus of these lecture.

2 Spectroscopy and topography with atomic contact control

A crucial role in a SMJ is played by the contacts. Different anchoring groups have been adopted to connect the molecule to the electrodes, ranging from thiol, to amine, or even fullerenes [23]. Also the direct contact of conjugated molecules with platinum electrodes have been investigated [24]. Correspondingly, a variety of mechanical stability and electronic coupling strengths have been reported. The common denominators and the technological challenge remains, though, the strong dependence of the transport characteristics on the precise contact configuration, down to the atomic scale.

As such, this strong contact dependence could undermine the reproducibility of the experimental results. Mainly, two approaches have been taken to overcome this problem, with completely opposite perspectives. On the one hand the break-junction technique averages over the contact fluctuations. Its goal is to identify the molecular fingerprints as persistent patterns in a statistical average of thousands of current traces [25–27]. On the contrary, ultra-high-vacuum low-temperature scanning tunneling microscopy minimizes the contact fluctuations. With this technique, also in combination with atomic force microscopy (AFM), one can achieve the most detailed characterization of both the tip [28] and the substrate electrodes. Even the position and orientation of the molecule with respect to the underlying crystal structure can be repeatedly monitored during the experiment.

Ideally, intrinsic electronic correlations are fully accessible only if both the spectrum and the eigenstates of a molecule are investigated within the same experiment. Scanning tunneling microscopy (STM) gives such a possibility [21, 22, 29–34] as one records the current by varying both the bias voltage and the tip position. Similarly to other electronic transport experiments [16, 18, 19, 35], the excitation spectrum is obtained by means of tunneling spectroscopy, i.e., by analyzing the peaks of the differential conductance. The current measured as a function of tip position gives, instead, access to the eigenstates. More precisely, the transitions between molecular many-body eigenstates are visualized, i.e., the quasiparticle wave function [36–39]

$$\phi(\mathbf{r}; N, E, E') = \langle N, E | \hat{\psi}(\mathbf{r}) | N+1, E' \rangle, \quad (2)$$

where N is the particle number on the molecule before the transition connecting states with energies E and E' , while $\hat{\psi}(\mathbf{r})$ is the electronic field operator. The quasiparticle wave function plays also an important role in the Liouville approach to transport theory which we will present in Sec. 3. If we express the field operator $\hat{\psi}(\mathbf{r})$ in terms of the complete set of the molecular orbitals (i.e., the eigenfunctions of the single-particle Hamiltonian), $\hat{\psi}(\mathbf{r}) = \sum_i \psi_i(\mathbf{r}) \hat{d}_i$, we see that the quasi-particle wave function coincides, for uncorrelated systems, with the molecular orbital, while deviations from this picture are expected as far as correlation steps in.

Particularly interesting to this extend, have been the realization of an STM with a thin insulating layer (a few monolayers) interposed between the molecule and the underlying metallic substrate. This technique, pioneered in the group of prof. G. Meyer [29], allows to select a single many-body transition and to visualize the corresponding quasiparticle wave function [22, 33]. The partial decoupling of the molecule from the metallic substrate enhances the intrinsic properties of the molecule. Recently, the concept has been further developed and measurements on insulators have been realized. The read-out of the electronic transitions is performed in the context of non contact atomic force microscopy [40].

3 Liouville approach to correlated transport

The problem of calculating the transport characteristics for a strongly interacting system coupled to leads still lacks a unifying solution able to cope with non-equilibrium boundary conditions in all transport regimes, despite great efforts to fill this gap [41–45]. Non-equilibrium Green's functions [46] remain the method of choice for systems with strong tunneling coupling to the leads, the interaction on the system been treated perturbatively. In the opposite limit, Liouville approaches [47] are the natural choice when the goal is the exact treatment of the strong correlated system, at the prize of a perturbative treatment of the tunneling coupling.

3.1 General transport theory

We briefly review here the second approach, which takes its name from the Liouville-von Neumann equation for the density matrix

$$\dot{\hat{\rho}} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}] \equiv \mathcal{L}\hat{\rho}, \quad (3)$$

where $\hat{\rho}$ is the density operator, $\mathcal{L}$ the Liouville superoperator and $\hat{H}$ the total Hamiltonian for the nanojunction. The latter can be split into the three components

$$\hat{H} = \hat{H}_{\text{mol}} + \hat{H}_{\text{leads}} + \hat{H}_{\text{tun}}, \quad (4)$$

where the $\hat{H}_{\text{mol}}$ describes the (strongly interacting) molecule, $\hat{H}_{\text{leads}}$ the (non interacting) leads and $\hat{H}_{\text{tun}}$ takes care of the tunneling coupling which transfers electrons between the leads and the molecule. Within this formal separation one envisages the purpose of the Liouville approach to derive, from the exact but intractable Eq. (3), an effective equation for the reduced

density operator $\hat{\rho}_{\text{red}} \equiv \text{Tr}_{\text{leads}} \hat{\rho}$, which describes only the evolution of the molecule, although in presence of the leads.

The molecule and the leads are taken as initially independent $\hat{\rho}(0) = \hat{\rho}_{\text{mol}}(0) \otimes \hat{\rho}_{\text{leads}}$ with the left and right lead in local thermal equilibrium

$$\hat{\rho}_{\text{leads}} = \frac{1}{Z_{G,L}} e^{-\beta(\hat{H}_L - \mu_L \hat{N}_L)} \otimes \frac{1}{Z_{G,R}} e^{-\beta(\hat{H}_R - \mu_R \hat{N}_R)}, \quad \mu_L - \mu_R = eV_{\text{bias}}, \quad (5)$$

where $\hat{H}_{\text{leads}} = \hat{H}_L + \hat{H}_R$, $\hat{N}_\eta$ is the particle number operator of lead $\eta = L, R$ with electrochemical potential μ_η , $Z_{G,\eta}$ is the grand canonical partition function, and V_{bias} is the potential drop across the junction. Entanglement between the molecule and the leads is induced by the tunneling dynamics. We concentrate, though, only on its influence onto the separable component of the density operator $\mathcal{P}\hat{\rho}(t) = \hat{\rho}_{\text{red}}(t) \otimes \hat{\rho}_{\text{leads}}$. The latter fulfills the following integro-differential equation of motion

$$\mathcal{P}\dot{\hat{\rho}}(t) = \mathcal{L}_{\text{mol}}\mathcal{P}\hat{\rho}(t) + \int_0^t \mathcal{K}(t-s)\mathcal{P}\hat{\rho}(s) ds \quad (6)$$

with the propagator kernel given by

$$\mathcal{K}(t-s) = \mathcal{P}\mathcal{L}_{\text{tun}} e^{(\mathcal{L}_{\text{mol}} + \mathcal{L}_{\text{leads}} + \mathcal{Q}\mathcal{L}_{\text{tun}}\mathcal{Q})(t-s)} \mathcal{L}_{\text{tun}} \mathcal{P}, \quad (7)$$

where we have introduced the projector operator $\mathcal{Q} = 1 - \mathcal{P}$ and the Liouvillian superoperators $\mathcal{L}_i = -\frac{i}{\hbar}[\hat{H}_i, \bullet]$ for each component of the Hamiltonian. See Appendix A for a derivation of Eq. (6) and (7). The latter are still exact and indicate, through the time dependent kernel, the emergence of memory in the molecular dynamics due to the coupling to the leads. This contribution, dissipative in the limit of large leads, adds to the time local coherent evolution of the isolated molecule represented by $\mathcal{L}_{\text{mol}}$. Differently from the Pauli master equation obtained by further approximations, Eq. (6), also called quantum master equation or Generalized Master Equation (GME) keeps coherences among molecular states essential, for example to capture interference effects even in the weak coupling limit [9, 11, 12, 48, 49].

The goal of a transport theory is the calculation of the electrical current through the system. The latter is formally derived starting from its definition of variation of the average particle number in the lead, $I_\eta(t) = e \frac{d\langle \hat{N}_\eta \rangle}{dt}$ with $\eta = L, R$, and reads

$$I_\eta(t) = \text{Tr} \left[\int_0^t \mathcal{K}_{I_\eta}(t-s) \mathcal{P}\hat{\rho}(s) ds \right], \quad (8)$$

where the trace is taken over the molecule *and* the leads Fock spaces. Moreover, the current kernel is written

$$\mathcal{K}_{I_\eta}(t-s) = \mathcal{P}\hat{I}_\eta e^{(\mathcal{L}_{\text{mol}} + \mathcal{L}_{\text{leads}} + \mathcal{Q}\mathcal{L}_{\text{tun}}\mathcal{Q})(t-s)} \mathcal{L}_{\text{tun}} \mathcal{P}, \quad (9)$$

where $\hat{I}_\eta$ is the time derivative of the number operator of lead η in the Heisenberg picture calculated at the initial time. From the expressions above it is clear how the formalism is ready to incorporate transient time dependent phenomena which arise due to the non-equilibrium condition induced by the leads. With some more effort even time dependent Hamiltonians can be included, but this goes beyond the scope of this lecture. We will analyze instead the

stationary limit (DC current) associated to a time independent bias voltage across the single-molecule junction. Due to the convolutive form of the kernels in Eq. (7) and (9) is it useful to go into the Laplace space. The stationary reduced density matrix is obtained, thanks to the final value theorem, as the solution of the equation

$$\left[\mathcal{L}_{\text{mol}} + \tilde{\mathcal{K}}(0) \right] \mathcal{P} \hat{\rho}(t \rightarrow \infty) = 0, \quad (10)$$

where, by definition of the Laplace transform, $\tilde{\mathcal{K}}(0) = \lim_{\lambda \rightarrow 0^+} \int_0^\infty e^{-\lambda t} \mathcal{K}(t) dt$. The stationary current thus reads

$$I_\eta(t \rightarrow \infty) = \text{Tr} \left[\tilde{\mathcal{K}}_{I_\eta}(0) \mathcal{P} \hat{\rho}(t \rightarrow \infty) \right]. \quad (11)$$

An explicit expression of the propagator and the current kernels depends on the specific form of the Hamiltonian. At this point it is useful to note that a systematic expansion of Eq. (7) and (9) in powers of the tunneling Liouvillian $\mathcal{L}_{\text{tun}}$ yields a consistent perturbation theory to be handled order by order within a diagrammatic approach [50]. Non perturbative effects like (energy dependent) level broadening due to quantum fluctuations, negative tunneling magnetoresistance [51, 52], and even precursors of the Kondo physics [42, 53, 54] have been obtained by infinite resummations of certain classes of diagrams.

3.2 Second-order perturbation

We consider here the second-order perturbation in the tunneling Hamiltonian which, as can be seen from Eq. (6), is the lowest non vanishing order in the propagator kernel. To fix the ideas, let us consider the following leads and tunneling Hamiltonians

$$\hat{H}_{\text{leads}} = \sum_{\eta \mathbf{k} \sigma} \varepsilon_{\eta \mathbf{k} \sigma} \hat{c}_{\eta \mathbf{k} \sigma}^\dagger \hat{c}_{\eta \mathbf{k} \sigma}, \quad (12)$$

with the momentum $\mathbf{k}$ and the spin σ of the quasi free electron in the lead η and

$$\hat{H}_{\text{tun}} = \sum_{\eta \mathbf{k} \sigma n p} p t_{\eta \mathbf{k} \sigma n}^p \hat{d}_{n \sigma}^p \hat{c}_{\eta \mathbf{k} \sigma}^{\bar{p}}, \quad (13)$$

where $p = \pm$ with the convention $\hat{c}^+ = \hat{c}^\dagger$ and $\hat{c}^- = \hat{c}$ and analogously for the operators $\hat{d}_{n \sigma}$ associated to the molecular orbital n with spin σ . The tunneling amplitudes $t_{\eta \mathbf{k} \sigma n}^p$, being proportional to the overlap of the lead and the molecule wave functions, keep track of the geometry of the contact. For them we define $t^+ = (t^-)^*$. Once the tunneling and the leads Hamiltonian are defined, we can calculate explicitly the action of the projection operators $\mathcal{P}$ in Eq. (7) and obtain the expression of the second-order kernel

$$\tilde{\mathcal{K}}^{(2)}(0) = -\frac{i}{2\pi} \sum_{\alpha_1 \alpha_2} \sum_{p \eta \sigma} \sum_{nm} \int \alpha_1 \alpha_2 \Gamma_{nm}^p(\varepsilon, \eta \sigma) \mathcal{D}_{n \sigma \alpha_2}^{\bar{p}} \frac{f_\eta^{(p \alpha_1)}(\varepsilon)}{p \varepsilon - i \hbar \mathcal{L}_{\text{mol}} + i 0^+} \mathcal{D}_{m \sigma \alpha_1}^p d\varepsilon. \quad (14)$$

The superoperators $\mathcal{D}_{n \sigma \alpha}^{\bar{p}}$ describe the action of a creation (annihilation) operator of the molecule when acting from the left ($\alpha = +1$) or from the right ($\alpha = -1$), i.e.,

$$\mathcal{D}_{n \sigma +}^p \hat{\rho} \equiv \hat{d}_{n \sigma}^p \hat{\rho}, \quad \mathcal{D}_{n \sigma -}^p \hat{\rho} \equiv \hat{\rho} \hat{d}_{n \sigma}^p.$$

The second-order kernel accounts for tunneling events in which only one lead at a time is involved. The direction of the tunneling event (to or from the lead maintained in local thermal equilibrium) is reflected in the Fermi distribution function, $f_{\eta}^{+}(\varepsilon) = 1/(1+e^{\beta(\varepsilon-\mu_{\eta})})$ and $f_{\eta}^{-}(\varepsilon) = 1-f_{\eta}^{+}(\varepsilon)$. Finally, the geometry of the contact is included in the single-particle rate-matrix $\Gamma^p(\varepsilon, \eta\sigma)$ which reads

$$\Gamma_{nm}^p(\varepsilon, \eta\sigma) = \frac{2\pi}{\hbar} \sum_{\mathbf{k}} t_{\eta\mathbf{k}\sigma n}^{\bar{p}} t_{\eta\mathbf{k}\sigma m}^p \delta(\varepsilon - \varepsilon_{\eta\mathbf{k}\sigma}). \quad (15)$$

By tracing Eq. (6) over the leads degrees of freedom and projecting on the (correlated) many-body eigenstates of $\hat{H}_{\text{mol}}$ we obtain a set of equation for the populations *and* coherences of the reduced density matrix, i.e., its diagonal and off-diagonal elements, respectively. The kernel $\tilde{\mathcal{K}}^{(2)}(0)$ and eventually also the current through the system is thus expressed in terms of many-body rates. For example,

$$R_{NE \rightarrow N+1 E'}^{\eta\sigma} = \sum_{nm} \langle NE | d_{n\sigma} | N+1 E' \rangle \Gamma_{nm}^{+}(E' - E, \eta\sigma) \langle N+1 E' | d_{m\sigma}^{\dagger} | NE \rangle f^{+}(E' - E - \mu_{\eta}) \quad (16)$$

is the rate of change of the population of the state with N particles and energy E due to transitions towards the state with $N+1$ particles and energy E' . For an STM set up with an s -symmetry tip, according to Chen's derivative rule [55], the tunneling amplitude is proportional to the molecular orbital at the tip position. The many-body rate in Eq. (16) is proportional to the modulus square of the quasi-particle wave function given in Eq. (2). Since the tip transitions are, typically, the bottle-neck of the electronic dynamics, the spatial dependence of the current will thus resemble the quasi-particle wave function. The latter reduces to the molecular orbital in absence of intrinsic correlations. Admixtures of p or d symmetry components of the tip wave-function enhance the corrugation in the imaging of the molecular states by introducing components of the current proportional to higher derivatives of the quasiparticle wave function [56]. Coherences in the density matrix become relevant only in presence of quasi-degenerate many-body levels ($\Delta E < \hbar\Gamma$) and for tunneling matrices associated to the leads which cannot be simultaneously diagonalized, i.e., in the absence of independent transport channels. It is under these conditions that many-body interference dominates the transport, leading to the formation of coherent trapping and dark states [12]. Under such conditions, the kernel $\tilde{\mathcal{K}}^{(2)}$ is also responsible of an effective internal dynamics, which is not described in terms of tunneling, but rather as a Lamb shift correction which adds to the molecule Hamiltonian [10, 48, 57, 58].

Summarizing, the most general equation of motion for the reduced density matrix, written up to second-order perturbation in the tunneling to the leads, reads

$$\dot{\hat{\rho}}_{\text{red}} = -\frac{i}{\hbar} [\hat{H}_{\text{mol}} + \hat{H}_{\text{LS}}^{(2)}, \hat{\rho}_{\text{red}}] + \mathcal{L}_{\text{tun}}^{(2)} \hat{\rho}_{\text{red}}. \quad (17)$$

Eq. (17) represents the starting point for the study of the intrinsic correlated transport phenomena presented in the next section.

The calculation of the spectrum and the many-body eigenstates of the molecular Hamiltonian is addressed within a mixed approach which aims, as much as possible, to combine the accuracy of

the ab-initio methods with the simplicity of the model. As a first step, a set of molecular orbitals is extracted from a tight binding model (or a DFT calculation). A limited set of N frontier orbitals is subsequently chosen for setting up a fully interacting Hamiltonian Eq. (1) which is diagonalized numerically in the complete 4^N dimensional Fock space. In this correlated many-body basis we evaluate the GME for the reduced density matrix, Eq.(17), and discuss the transport phenomena which characterize the different single-molecule junctions.

4 Examples of intrinsic correlated transport phenomena

4.1 Dynamical spin crossover

As a first example of a correlated phenomenon we consider the spin crossover induced on a metal-organic molecule under non-equilibrium conditions. Spin-crossover metal-organic compounds play a prominent role [14–16, 19, 59] in the emergent field of molecular spintronics. Spin crossover is the transition between metastable spin states under the influence of external stimuli [60]. The many-body exchange interaction of the d -electrons on the metal center, in combination with the crystal field generated by the surrounding ligand, determines their spin state. In three-terminal devices, the gate electrode used to tune the charge also governs the associated spin state [16, 19, 59]. Metal-organic molecules have also come in the focus of STM experiments [14, 15, 32]. More generally, the role itself of many-body effects in STM single-molecule junctions is receiving increasing attention, both theoretically [33, 37–39, 57] and experimentally [14, 15, 21, 33].

In this section we demonstrate the appearance of a non-equilibrium high-spin state in CuPc on an insulating substrate caused by many-body correlations. We illustrate that, for a given substrate work-function, it is possible to control the effective ground state of the molecule by varying the tip position or the bias voltage across the junction. The only requirements for this genuine many-body effect are an asymmetry between tip and substrate tunneling rates, which is naturally inherent to STM setups, and an energetic proximity of an excited neutral state of the molecule to its anionic ground state. As discussed below, the experimental set-up is similar to that of Ref. [21], but with a slightly larger work-function for the substrate. Control over the work-function can be achieved by choosing different materials or crystallographic orientation for the substrate, with effects analogous to a discrete gating of the molecule. Several approaches to gate an STM junction have been also recently investigated [61–63].

Many-body Hamiltonian and spectrum of CuPc: To properly describe the many-body electronic structure of CuPc is by itself a nontrivial task, since the relatively large size of the molecule makes it impossible to diagonalize exactly a many-body Hamiltonian written in a local, atomic basis as done for smaller molecules [9, 64, 65]. STM transport experiments on single-molecules, however, are restricted to an energy window involving only the low-lying states of the molecule in its neutral, cationic and anionic configuration, with the equilibrium configuration at zero bias set by the work-function ϕ_0 of the substrate [21]. This allows one to use a restricted basis of frontier orbitals to construct the many-body Hamiltonian [20, 66]. For example, for a copper

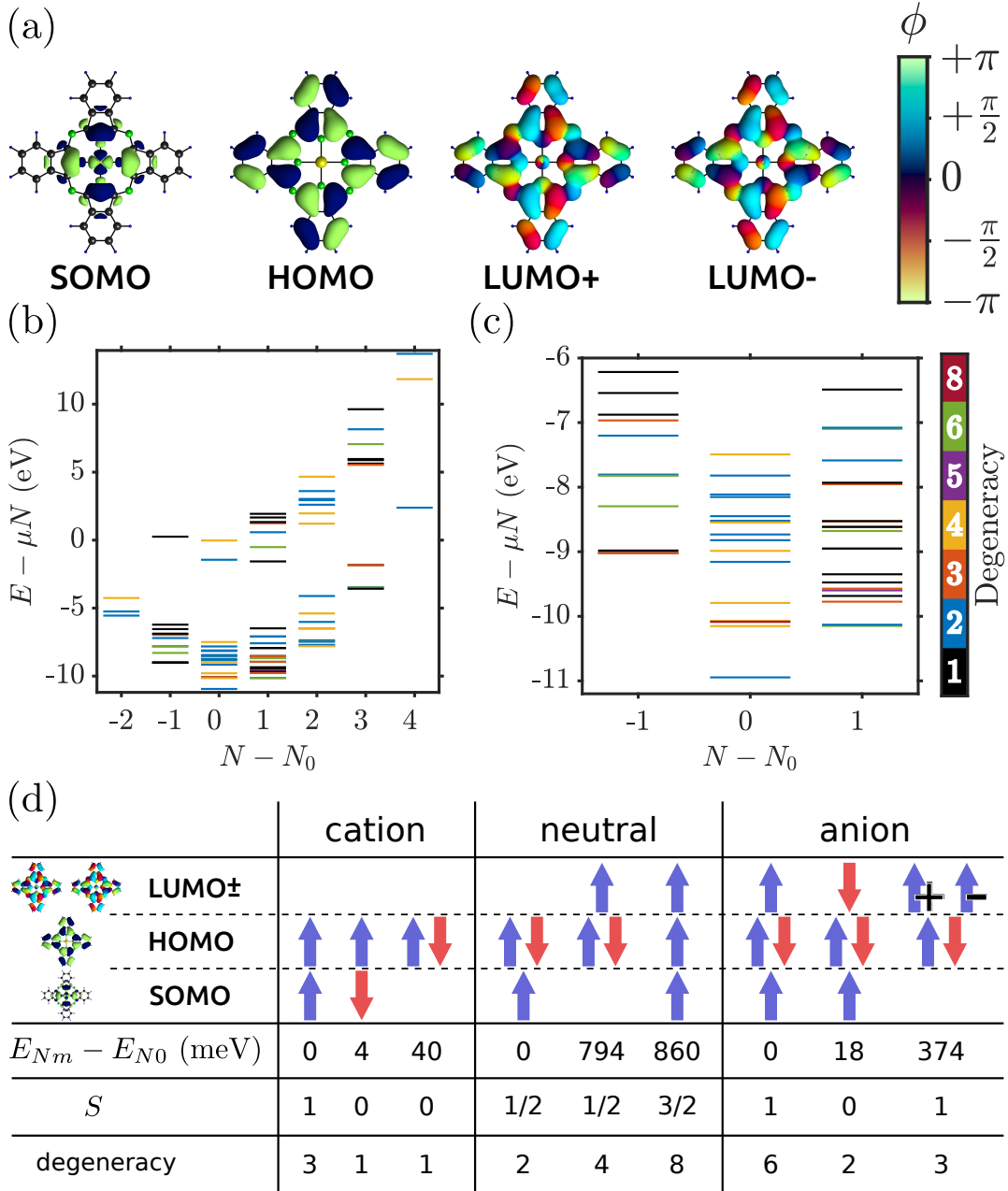


Fig. 1: (a) Frontier orbitals used for the many-body calculation, in their complex representation. The color code shows the phase of the wavefunctions. (b), (c) Full and low-energy cutout, respectively, of the many-body spectrum of CuPc at chemical potential $\mu = -4.65$ eV. (d) Scheme of the lowest-lying many-body states. From [17].

substrate as in [21] is $\phi_0 = 4.65$ eV, and CuPc in equilibrium is in its neutral ground state. Thus, in the following we only retain four frontier orbitals of CuPc, the SOMO (S), the HOMO (H) and the two degenerate LUMO ($L^\pm$) orbitals, see Fig. 1(a). In equilibrium, the molecule contains $N_0 = 3$ frontier electrons. In this basis, *all* matrix elements of the Coulomb interaction are retained. Hence, besides Hubbard-like density-density interaction terms, our model also includes exchange and pair hopping terms, which ultimately are important for the structure and spin configuration of the molecular excited states.

The Hamiltonian of CuPc in the basis of the four single-particle frontier orbitals reads

$$\hat{H}_{\text{mol}} = \sum_i \tilde{\varepsilon}_i \hat{n}_i + \frac{1}{2} \sum_{ijkl} \sum_{\sigma\sigma'} V_{ijkl} \hat{d}_{i\sigma}^\dagger \hat{d}_{j\sigma'}^\dagger \hat{d}_{k\sigma'} \hat{d}_{l\sigma}, \quad (18)$$

where $i = S, H, L\pm$ and σ is the spin degree of freedom. The energies $\tilde{\varepsilon}_i = \varepsilon_i + \Delta_i$ contain the single-particle molecular energies ε_i obtained from diagonalizing the single-particle Hamiltonian $\hat{H}_0$ of CuPc, $\varepsilon_S = -12.0$ eV, $\varepsilon_H = -11.7$ eV, and $\varepsilon_{L\pm} = -10.7$ eV. The parameters Δ_i account for crystal-field corrections and the ionic background of the molecule, since the atomic onsite energies in $\hat{H}_0$ come from Hartree-Fock calculations for isolated atoms [67]. The Δ_i are free parameters of the theory. Isolated CuPc has D_{4h} symmetry; the four molecular orbitals $|i\sigma\rangle$ that make up the basis of Eq. (18) transform like its b_{1g} (S), a_{1u} (H) and e_u ($L^\pm$) representations. As a consequence, they acquire distinct phases ϕ_i when rotated by 90 degrees around the main symmetry axis of the molecule, as illustrated in Fig. 1(a). This yields an easy rule to determine the nonvanishing Coulomb matrix elements V_{ijkl} in Eq. (18): $V_{ijkl} \neq 0$ if $\phi_i + \phi_j - \phi_k - \phi_l = 0 \bmod 2\pi$, i.e., non-vanishing contributions are only possible if the phases of the corresponding molecular orbitals add up to multiples of 2π . These considerations remain true in the presence of a homogenous substrate, which reduces the symmetry to C_{4v} . For a detailed discussion concerning the parametrization of Eq. (18) we refer to the supplemental material of [17]. Exact numerical diagonalization of $\hat{H}_{\text{mol}}$ finally yields the many-body eigenenergies E_{Nm} and eigenstates $|Nm\rangle$ of the molecule, labeled by particle number N and state index m .

Since the molecule is in contact with the substrate and is able to exchange electrons, it is necessary to consider a grand canonical ensemble $\hat{H}_{\text{mol}} - \mu\hat{N}$, where μ is the chemical potential of the substrate, which is given by its negative work-function, $\mu = -\phi_0$. Moreover, the presence of the leads renormalizes the Hamiltonian $\hat{H}_0$ due to image-charge effects [65, 68]. We model these effects with an effective Hamiltonian $\hat{H}_{\text{mol-env}} = -\delta_{\text{ic}}(\hat{N} - N_0)^2$, with $\hat{N}$ the particle-number operator on the system and δ_{ic} obtained from electrostatic considerations. To fit our spectrum to the experiment of Swart et al. [21], which was taken on a copper substrate Cu(100) ($\phi_0 = 4.65$ eV) on a trilayer of NaCl, we used a constant shift $\Delta_i = \Delta = 1.83$ eV, a dielectric constant $\varepsilon_{\text{mol}} = 2.2$ in the evaluation of the matrix elements V_{ijkl} , and an image-charge renormalization $\delta_{\text{ic}} = 0.32$ eV.

Figures 1(b), (c) show the cationic, neutral, and anionic subblocks of the many particle spectrum and their degeneracies. A schematic depiction of these states is shown in Fig. 1(d). As the actual states are linear combinations of several Slater determinants, only dominant contributions are shown. The neutral groundstate has a doublet structure (with total spin $S = \frac{1}{2}$) coming from the doubly filled HOMO and the unpaired spin in the SOMO. The cationic and anionic groundstates have triplet structures ($S = 1$). The former has a singly filled HOMO, the latter a singly filled LUMO orbital which form spin triplets (and singlets, $S = 0$, for the first excited states) with the singly filled SOMO. Importantly, the orbital degeneracy of the LUMO makes up for an additional twofold multiplicity of the anionic ground and first excited states. The first excited state of the neutral molecule is found to be also a doublet ($S = \frac{1}{2}$) with additional twofold

orbital degeneracy. Finally, the second excited state shows a spin quadruplet structure ($S = \frac{3}{2}$) together with twofold orbital degeneracy.

Transport dynamics and spin crossover: The full system is characterized by the Hamiltonian $\hat{H} = \hat{H}_{\text{mol}} + \hat{H}_{\text{mol-env}} + \hat{H}_{\text{S}} + \hat{H}_{\text{T}} + \hat{H}_{\text{tun}}$, where $\hat{H}_{\text{S}}$ and $\hat{H}_{\text{T}}$ are describing non-interacting electronic reservoirs for substrate (S) and tip (T). The tunneling Hamiltonian is $\hat{H}_{\text{tun}} = \sum_{\eta\mathbf{k}i\sigma} t_{\eta\mathbf{k}i} \hat{c}_{\eta\mathbf{k}\sigma}^\dagger \hat{d}_{i\sigma} + \text{h.c.}$, where $\hat{c}_{\eta\mathbf{k}\sigma}^\dagger$ creates an electron in lead η with spin σ and momentum $\mathbf{k}$. The tunneling matrix elements $t_{\eta\mathbf{k}i}$ are obtained analogously to Ref. [57]. The dynamics is calculated via a generalized master equation for the reduced density operator $\rho_{\text{red}} = \text{Tr}_{\text{S,T}}(\rho)$, see Refs. [9, 57]. In particular, we are interested in the state ρ_{red}^∞ solving the stationary equation $\mathcal{L}[\rho_{\text{red}}] = 0$, where $\mathcal{L}$ is the Liouvillian superoperator.

In analogy to Ref. [69] we included a phenomenological relaxation term $\mathcal{L}_{\text{rel}}$ in the Liouvillian¹

$$\mathcal{L}_{\text{rel}}[\hat{\rho}] = -\frac{1}{\tau} \left(\hat{\rho} - \sum_{Nm} \rho_{mm}^{\text{th},N} |Nm\rangle \langle Nm| \sum_n \rho_{nn}^N \right). \quad (19)$$

It is proportional to the deviation of the reduced density matrix from the thermal one, ρ^{th} , which is given by the Boltzmann distribution $\rho_{mm}^{\text{th},N} \sim \exp\left(-\frac{E_{Nm}}{k_B T}\right)$ with $\sum_m \rho_{mm}^{\text{th},N} = 1$. Since $\mathcal{L}_{\text{rel}}$ describes relaxation processes which conserve the particle number on the molecule, it does not contribute directly to the current. The relaxation factor $1/\tau$ is taken of the same order of magnitude as the tip tunneling rate. The stationary current through the system is evaluated from

$$\langle \hat{I}_{\text{S}} + \hat{I}_{\text{T}} \rangle = \frac{d}{dt} \langle \hat{N} \rangle = \text{Tr}_{\text{mol}} \left(\hat{N} \mathcal{L}[\hat{\rho}_{\text{red}}^\infty] \right) \equiv 0. \quad (20)$$

The Liouvillian $\mathcal{L} = \mathcal{L}_{\text{rel}} + \sum_{\eta} \mathcal{L}_{\eta}$ decomposes into the relaxation term and sub-Liouvillians for each lead. Sorting the occurring terms in Eq. (20) into substrate and tip contributions yields the current operator of the respective lead η as $\hat{I}_{\eta} = \hat{N} \mathcal{L}_{\eta}$.

Results of our transport calculations are presented in Fig. 2. In panels (a,d,g) we show constant height current maps, constant current STM images in (b,e,h) and in (c,f,i) maps of the expectation value of the total spin of the molecule depending on tip position, $S_{\text{rT}} = \sqrt{\langle \hat{S}^2 \rangle_{\text{rT}} + \frac{1}{4}} - \frac{1}{2}$ where $\langle \hat{S}^2 \rangle_{\text{rT}} = \text{Tr}_{\text{mol}} \left(\hat{S}^2 \hat{\rho}_{\text{red}}^\infty(\mathbf{r}_{\text{T}}) \right)$. The constant height and spin maps are each taken at a tip-molecule distance of 5 Å. The upper three panels (a,b,c) are for a work-function of $\phi_0 = 4.65$ eV and a bias voltage of $V_b = -2.72$ V. At this position the cationic resonance is occurring. Since the difference between neutral and cationic groundstate is the occupation of the HOMO (see Fig. 1(d)), tunneling occurs via this orbital, and the current maps (a,b) resemble its structure. With the same work function, $\phi_0 = 4.65$ eV, the anionic resonance is taking place at the positive bias $V_b = 0.81$ V, see Fig. 2(d,e). For equivalent reasons as in the former case, tunneling is happening via the LUMO and the spatial dependence of the current resembles the topography of this orbital. Panels (g,h,i) instead are recorded at $\phi_0 = 5.2$ eV, again at the anionic resonance which is now shifted to $V_b = 1.74$ V due to the larger work-function. Panel (g) is puzzling. Despite being an anionic resonance, it closely resembles the HOMO, cf. panels (a),(b). A closer

¹Differently from Ref. [69] we have included in Eq. (19) also the coherences. $\mathcal{L}_{\text{rel}}$ accounts thus also for dephasing. For simplicity, we assume the same phenomenological rate for dephasing and dissipation.

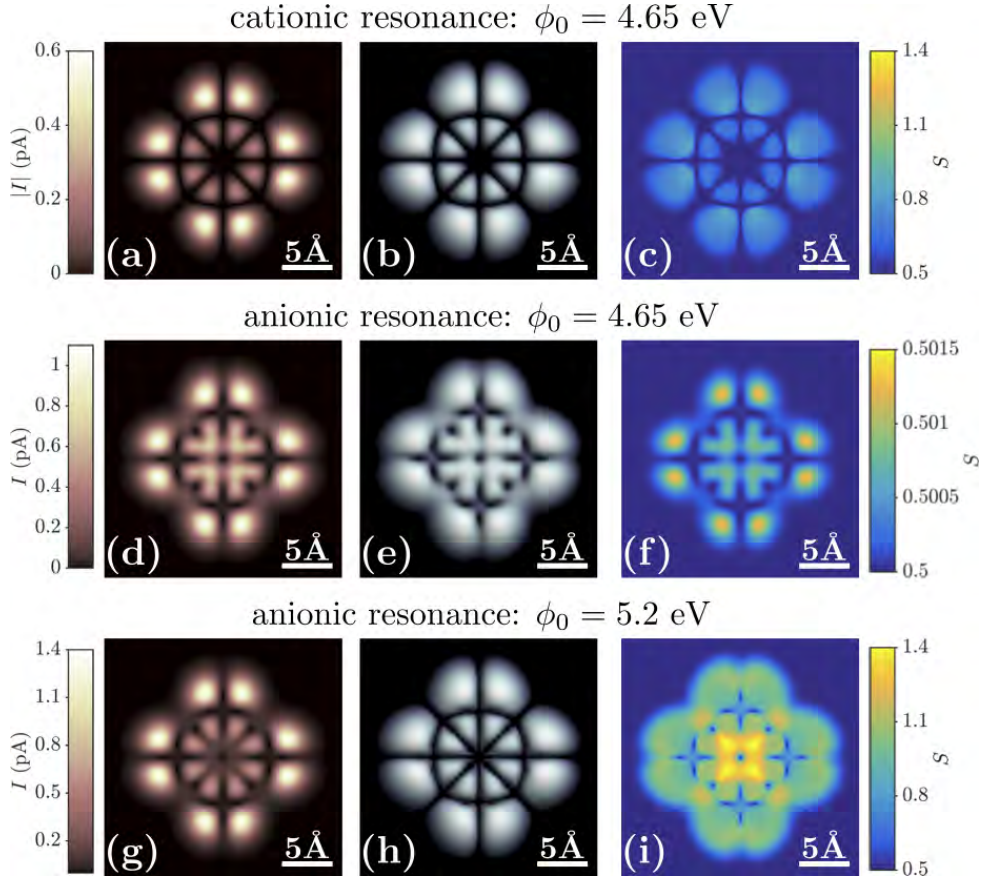


Fig. 2: (Constant height current maps (a,d,g), constant current maps (b,e,h) and maps of the system's total spin S (c,f,i). Constant height and spin maps are taken at a tip-molecule distance of 5 Å, constant current maps at currents $I = 0.5, 0.75$, and 1.0 pA for panels (c), (f), and (i), respectively. From [17].

inspection reveals also a likeness to the LUMO (see panel (d)) but with additional diagonal nodal planes, matching the nodal plane structure of the HOMO. When observing the constant current map in panel (h), and comparing it with panels (b) and (e), this statement becomes more evident. This anomalous topography can not be explained by single orbital tunneling.

Panels (c), (f) and (i) reveal the tip-position dependent expectation value of the total spin. At the standard anionic transition, panel (f), the spin remains essentially constant. At the standard cationic transition, panel (c), the rather homogeneous enhancement of the molecular spin is due to small populations of a large number of excited states, made accessible by the large resonance bias ($V_{\text{res}} = -2.7$ V). The anomalous anionic transition, panel (i), shows the largest variation of the molecular spin, concentrated at the positions of the anomalous current suppression, compare panels (g) and (d). To explain the unconventional properties shown in Fig. 2, we examine bias traces taken at different tip positions and values of the work-function. Figure 3(a) shows a shift of the anionic resonant peak in the $\frac{dI}{dV}$ for the anomalous case. The value V_{res} at which the peak is expected is given by

$$V_{\text{res}}(\phi_0) = \frac{1}{\alpha_{\text{T}}|e|} (E_{N_0+1,0} - E_{N_0,0} - \delta_{\text{ic}} + \phi_0), \quad (21)$$

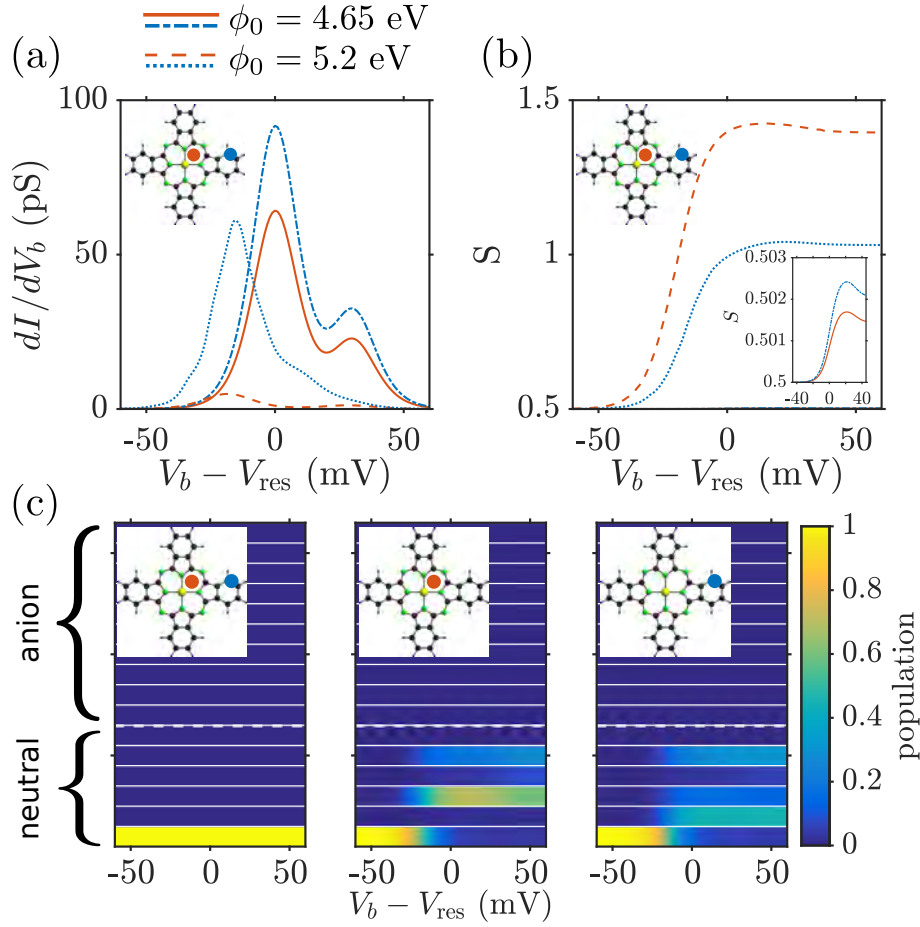


Fig. 3: (a) Differential conductance and (b) total spin curves taken at different tip positions and work-functions around the bias $V_{\text{res}}(\phi_0)$ of the anionic resonance. The inset in (b) shows the change of the spin for the standard case in magnification. (c) Populations of the density matrix around $V_{\text{res}}(\phi_0)$. Left panel: standard case, $\phi_0 = 4.65$ eV. Middle (right) panel: anomalous case, $\phi_0 = 5.2$ eV, with tip near the center (outer on the ligand). From [17].

where α_T is the fraction of bias drop between tip and molecule, and $E_{N,0}$ is the energy of the N -particle ground state. The shift of the resonance to lower biases seen in Fig. 3(a) suggests the appearance of a population inversion from the neutral ground state to an excited state. Transitions from the latter to the anionic ground state open in fact at much lower biases. Also the evolution of the spin of the molecule shown in Fig. 3(b) reinforces this proposition. In the anomalous case, the change of the system from a low to a high spin state, as well as the saturation of the spin, can be clearly seen. This contrasts with the normal anionic transition, where only a marginal change is observable. In Fig. 3(c) we show the evolution of the eigenvalues of the stationary density matrix ρ_{red}^∞ , i.e., the populations of the physical basis [9], around the anionic resonance $V_{\text{res}}(\phi_0)$, depending on work-function and tip position. In the standard case (left panel of Fig. 3(c)), the ground state of the system is always the neutral ground state. For the anomalous case (middle and right panels of Fig. 3) however, the picture changes dramatically, as there is a remarkable depopulation of the neutral ground state in favor of different excited states, depending on the position of the tip.

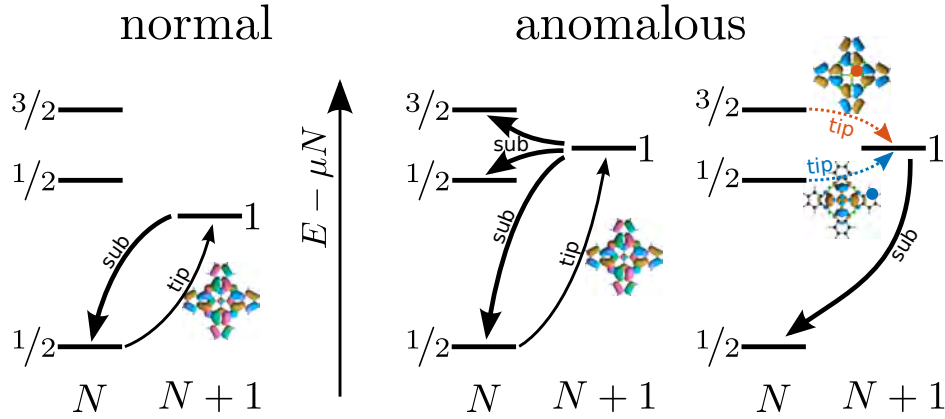


Fig. 4: Simplified sketch of the tunneling processes at the anionic resonance for the standard ($\phi_0 = 4.65$ eV) and the anomalous ($\phi_0 = 5.2$ eV) case. In the latter, population inversion takes place. The colors of the arrows denote tip positions where the corresponding transition acts as a bottleneck: Orange (blue) stands for the center (the outer ligand) of CuPc. From [17].

We focus now on the mechanism yielding the population inversion with associated spin crossover. In the standard case, at sufficiently high bias, the transition from the neutral to the anionic groundstate is opening, and tunneling of an electron into the LUMO brings the molecule into the anionic ground state. By consecutive tunneling to the substrate, the system goes back into its neutral ground state, see Fig. 4 for a simple sketch. Since the tunneling rates to the substrate are much larger than their tip counterparts, the system stays essentially in the neutral ground state with spin $S = \frac{1}{2}$. Also in the anomalous case an initial tunneling event brings the molecule into the anionic ground state. However, from there, due to finite temperature and proximity of the many-body eigenenergies, the system has a finite probability to go into a neutral excited state by releasing an electron to the substrate. The position of the tip and the structure of these excited states themselves then determine the stationary state: The molecule can only return to its neutral ground state by successive transitions to the anionic ground state via the tip, and from there to the neutral ground state via the substrate. However, the former process acts as a bottleneck and depends on the tip position. Leaving the first excited state ($S = \frac{1}{2}$) requires tunneling into the SOMO, while leaving the second excited state ($S = \frac{3}{2}$) would require tunneling into the HOMO. Additionally, near the center of the molecule the HOMO is vanishing, whereas on the outer ligand part the SOMO has little to no amplitude. Therefore, tunneling into these orbitals at the respective positions is strongly suppressed and the system ultimately ends up in the corresponding neutral excited states.

In synthesis, for an experimentally accessible substrate work-function of $\phi_0 = 5.2$ eV, we predict the appearance, in proximity to the anionic resonance, of a population inversion between the neutral ground and excited states of CuPc. Depending on the tip position, the molecule is triggered into a low-spin ($S=1/2$) to high-spin ($S=3/2$) transition which is mediated by this population inversion. This inversion is experimentally observable via dramatic changes in the topographical properties of constant height and constant current STM images, compared to a

standard LUMO-mediated anionic transition. Direct observation of the spin crossover might be accessible using spin-polarized scanning probe microscopy techniques. [70] The effect is also robust against moderate charge conserving relaxation processes. The quantitative accuracy of the spectroscopic and topographical results presented here is limited by the adopted semiempirical model. The spin crossover with the associated anomalous topography of the anionic resonance depends, however, on qualitative properties of the many-body spectrum and of the molecular orbitals. Thus, despite our focus on CuPc, they should be observable also in other molecules with comparable frontier orbital structure.

4.2 Apparent orbital reversal

In general, Coulomb charging energies strongly depend on the localization of electrons and hence on the spatial extent of the orbitals they occupy. Therefore the orbital sequence of a given molecule can reverse upon electron attachment or removal, if some of the frontier orbitals are strongly localized while others are not, like in phthalocyanines [30, 71–74]. Coulomb interaction may also lead to much more complex manifestations such as quantum entanglement of delocalized molecular orbitals.

Here we show, that the energy spacing of the frontier orbitals in a single-molecular wire of individual dicyanovinyl-substituted quinquethiophene (DCV5T) can be engineered to achieve near-degeneracy of the two lowest lying unoccupied molecular orbitals, leading to a strongly-entangled ground state of DCV5T^{2-} . These orbitals are the lowest two of a set of particle-in-a-box-like states and differ only by one additional nodal plane across the center of the wire. Hence, according to the fundamental oscillation theorem of Sturm-Liouville theory their sequence has to be set with increasing number of nodal planes, which is one of the basic principles of quantum mechanics [75, 76]. This is evidenced and visualized from scanning tunneling microscopy (STM) and spectroscopy (STS) of DCV5T on ultrathin insulating films. Upon lowering the substrate's work function, the molecule becomes charged, leading to a reversal of the sequence of the two orbitals. The fundamental oscillation theorem seems strikingly violated since the state with one *more* nodal plane appears *lower* in energy. This contradiction can be solved, though, by considering intramolecular correlation leading to a strong entanglement in the ground state of DCV5T^{2-} .

We refer to experiments carried out in the group of J. Repp, with a home-built combined STM/atomic force microscopy (AFM) using a qPlus sensor [77] operated in ultra-high vacuum. Bias voltages are applied to the sample. All AFM data, dI/dV spectra and maps, were acquired in constant-height mode. Calculations of the orbitals and effective single-particle electronic structure were performed within the density functional theory (DFT) as implemented in the SIESTA code [78] and are based on the generalized gradient approximation (GGA-PBE). The many-body eigenstates are determined from a diagonalization of the many-body model Hamiltonian H_{mol} , similar to the one introduced in Eq. (1). Based on these, STM-image and spectra simulations were performed within a Liouville approach for the density matrix ρ , as presented in section 3.

Control of the level spacing: The molecular structure of DCV5T, shown in Fig. 5a, consists of a quinquethiophene (5T) backbone and a dicyanovinyl (DCV) moiety at each end. The delocalized electronic system of polythiophene and oligo-thiophene enables conductance of this material [79–81]. The lowest unoccupied orbital of each of the thiophene rings couples electronically to its neighbors and forms a set of particle-in-a-box-like states [82,83]. The LUMO to LUMO+1 level spacing of the quinquethiophene (5T) backbone is approx. 0.7 eV [82], which is in good agreement with the energy difference calculated for free 5T based on DFT, as shown in Fig. 5a, left. This DFT-based calculation also confirms the nature of the LUMO and LUMO+1 orbitals, both deriving from the single thiophene’s LUMOs and essentially differing only by one additional nodal plane across the center of the molecule. To enable the emergence of correlation and thus level reordering, we have to bring these two states closer to each other. This is achieved by substituting dicyanovinyl moieties with larger electron affinity at each end of the molecular wire. As the orbital density of the higher lying particle-in-a-box-like state, namely LUMO+1, has more weight at the ends of the molecule, it is more affected by this substitution than the lowest state, the LUMO. This is evidenced by corresponding calculations of DCV5T, for which the LUMO to LUMO+1 energy difference is reduced by more than a factor of two, see Fig. 5a, left. The increased size of DCV5T may also contribute to the reduced level spacing. For the rest of this section, we concentrate on the LUMO and LUMO+1 orbitals only. To avoid confusion, we refrain from labeling the orbitals according to their sequence but instead according to their symmetry with respect to the mirror plane perpendicular to the molecular axis, as symmetric (S) and antisymmetric (AS). Hence, the former LUMO and the LUMO+1 are the S and AS states, respectively.

Apparent orbital reversal: To study the energetic alignment of the orbitals as well as their distribution in real space, ultrathin NaCl insulating films were employed to electronically decouple the molecules from the conductive substrate [29]. It has been shown that in these systems the work function can be changed by using different surface orientations of the underlying metal support [21, 29, 84]. Importantly, this does not affect the (100)-terminated surface orientation of the NaCl film, such that the local chemical environment of the molecule remains the same, except for the change of the work function.

However, in the present case, this alone has a dramatic effect on the electronic structure of the molecular wires as is evidenced in Fig. 5b. There, the STM images are shown for voltages corresponding to the respective lowest lying molecular resonances at positive sample voltage for DCV5T adsorbed on NaCl/Cu(111) (top panel) and NaCl/Cu(311) (bottom panel). They both show a hot-dog like appearance of the orbital density, in which a central lobe is hidden inside outer lobes, as was discussed, for example, in [13, 82]. However, whereas the orbital density of DCV5T/NaCl/Cu(311) shows a clear depression at the center of the molecule, indicating a nodal plane, DCV5T/NaCl/Cu(111) does not. Apparently, the energetically lowest lying state is not the same for the two cases, but S for DCV5T/NaCl/Cu(111) and AS in the case of DCV5T/NaCl/Cu(311). In contrast, STM images, acquired at voltages well below the first resonance, reflect the geometry of the molecule in both cases as wire-like protrusion (see insets of Fig. 5b).

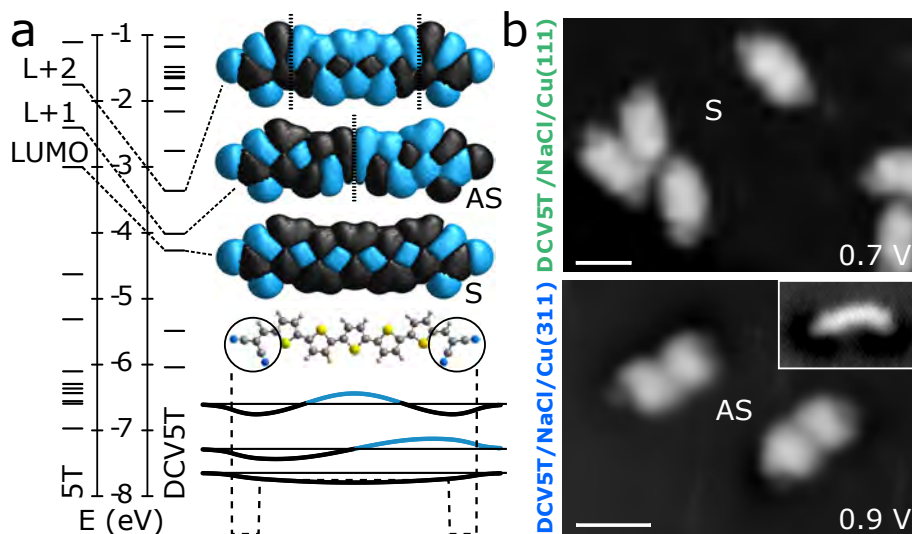


Fig. 5: (a) Molecular structure and density-functional theory based calculations of the electronic structure of 5T and DCV5T. The panel depicts the molecular structure, the calculated orbitals and energies for the LUMO, LUMO+1 and LUMO+2 as indicated. The orbitals are depicted as contours of constant probability density. The LUMO and LUMO+1 orbitals derive from the thiophene subunit's LUMO. They are the lowest two of a set of particle-in-a-box-like states and differ only by one additional nodal plane. Whereas the LUMO to LUMO+1 energy difference is approx. 0.7 eV for 5T, this difference is drastically reduced for DCV5T. The basic principle of level engineering is illustrated for a one-dimensional quantum box. (b) STM images of the first DCV5T electronic resonance on NaCl/Cu(111) (top) and NaCl/Cu(311) (bottom). The inset shows an STM image at a voltage below the first molecular resonance. From [22].

We hence assume that the molecules are neutral on NaCl/Cu(111) and that the S state corresponds to the LUMO. According to the literature, changing the copper surface orientation from Cu(111) to Cu(311) results in a lowering of the work function by approximately 1 eV [29, 85, 86]. Hence, one may expect that the former LUMO, initially located 0.7 eV above the Fermi level E_F in the case of NaCl/Cu(111) will shift to below the Fermi level [21, 30] for NaCl/Cu(311) such that the molecule becomes permanently charged.

To obtain a systematic understanding of the level alignment of the S and AS states of the molecule on both substrates, differential conductance (dI/dV) spectra and dI/dV -maps on DCV5T molecules have been acquired. Typical spectra measured at the center and the side of the molecule are shown in Figs. 6a and b on NaCl/Cu(111) and NaCl/Cu(311), respectively. DCV5T exhibits two dI/dV resonances at positive bias but none at negative voltages down to -2.5 V. According to the dI/dV maps and consistent with the different intensities in the spectra acquired on and off center of the molecule, the S state at $\simeq 0.7$ V is lower in energy than the AS state occurring at $\simeq 1.1$ V. The energy difference of $\simeq 0.4$ eV is in rough agreement to our calculations (see Fig. 5a). As discussed above, in the case of NaCl/Cu(311), DCV5T exhibits the AS state as the lowest resonance at positive bias voltages, this time at $\simeq 0.9$ V. This is additionally evidenced by the constant-current STM image and the corresponding dI/dV map in Fig. 6b. The S state is now located at higher voltages, namely at $\simeq 1.3$ V, as seen in the

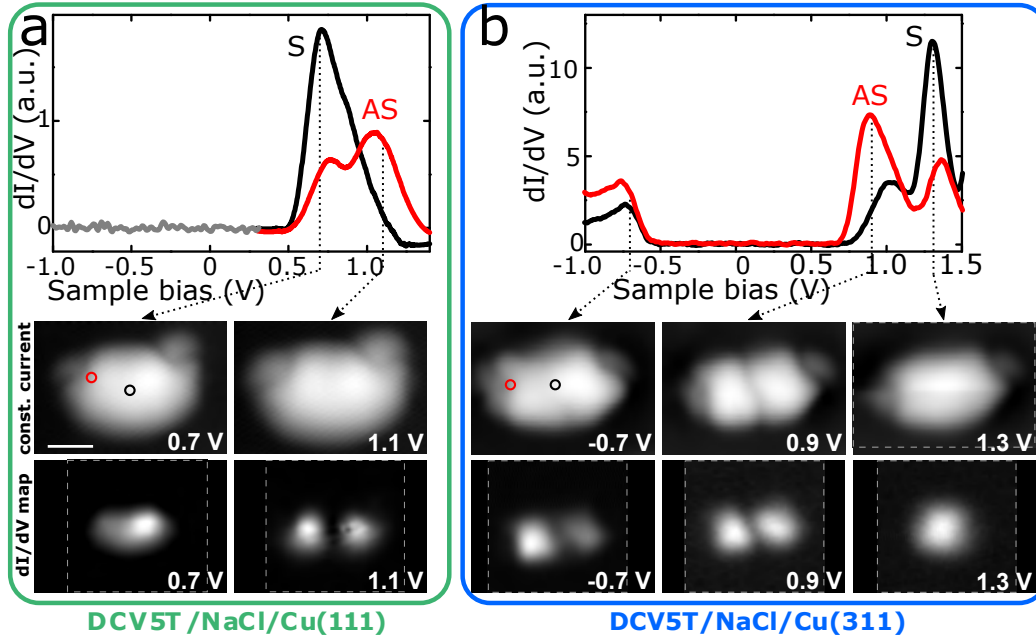


Fig. 6: dI/dV spectra (top panels), constant-current STM images (center panels) and dI/dV maps (bottom panels) on the individual molecule DCV5T on NaCl/Cu(111) (a) and NaCl/Cu(311) (b) respectively. The resonances are labelled with S and AS, referring to the symmetric and antisymmetric states, respectively. dI/dV spectra were recorded on (black) and off (red) the center of the molecule as indicated by dots in the STM images. The spatial distribution of orbitals gives rise to the different intensities at different tip positions as depicted in the inset. To not miss any small dI/dV signals in the low-bias range, a corresponding spectrum (grey) was measured with the tip being $\simeq 2 \text{ \AA}$ closer to the surface compared to the other two (red and black). All spectra were slightly low-pass filtered. The negative differential conductance beyond the AS peak (black curve) can be attributed to the increase in the tunneling barrier height with increasing bias voltage [29]. The images are resized to have the same size and scale, whereby the area of measured data is indicated with white dashed rectangles. Constant current images $I = 2.4 \text{ pA}$; bias voltage as indicated. Scale bar 1 nm. From [22].

spectrum and the dI/dV map. Obviously, the two states are reversed in their sequence. In this case, at negative bias voltages, a peak in dI/dV indicates an occupied state in equilibrium, in stark contrast to DCV5T/NaCl/Cu(111) but in agreement with the assumption of the molecule being negatively charged. The constant-current image acquired at -0.7 V , corresponding to the first peak at negative bias, seems to be a superposition of both the S and AS states.

The experimentally observed reversal of the orbital sequence is in striking disagreement with the fundamental oscillation theorem. To understand this apparent orbital reversal we go beyond the single-particle picture and invoke the role of electronic correlations. In the double-barrier tunneling junction geometry employed here, the resonances in dI/dV are associated with a temporary change of electron number on the molecule. In this terms the two peaks of DCV5T/NaCl/Cu(111) at positive bias are $\text{DCV5T} \leftrightarrow \text{DCV5T}^-$ transitions (see Fig. 7), and, in the same spirit, the ones of DCV5T/NaCl/Cu(311) at positive and at negative bias should be interpreted as $\text{DCV5T}^{2-} \leftrightarrow \text{DCV5T}^{3-}$ and $\text{DCV5T}^{2-} \leftrightarrow \text{DCV5T}^-$ transitions, respectively.

Many-body Hamiltonian and entangled ground state: Both the topographical and the spectroscopic data presented so far suggest that the electronic transport through DCV5T involves, in the present bias and work-function ranges, only the symmetric (S) and the antisymmetric (AS) orbitals. We concentrate on them and freeze the occupation of the other lower (higher) energy orbitals to 2 (0). In terms of these S and AS *frontier* orbitals we write the minimal interacting Hamiltonian for the isolated molecule

$$H_{\text{mol}} = \varepsilon_S \hat{n}_S + \varepsilon_{AS} \hat{n}_{AS} + \frac{U}{2} \hat{N}(\hat{N} - 1) + J \left(\sum_{\sigma\sigma'} \hat{d}_{AS\sigma}^\dagger \hat{d}_{S\sigma'}^\dagger \hat{d}_{AS\sigma'} \hat{d}_{S\sigma} + \hat{d}_{AS\uparrow}^\dagger \hat{d}_{AS\downarrow}^\dagger \hat{d}_{S\downarrow} \hat{d}_{S\uparrow} + \hat{d}_{S\uparrow}^\dagger \hat{d}_{S\downarrow}^\dagger \hat{d}_{AS\downarrow} \hat{d}_{AS\uparrow} \right), \quad (22)$$

where $\hat{d}_{S(AS)\sigma}^\dagger$ creates an electron with spin σ in the symmetric (antisymmetric) orbital, $\hat{n}_i$ counts the number of electrons in the orbital with $i = S, AS$ and $\hat{N}$ represents the total number of electrons occupying the two frontier orbitals. The interaction parameters $U = 1.4$ eV and $J = 0.75$ eV are obtained from the DFT orbitals by direct calculation of the associated Coulomb integrals and assuming a dielectric constant $\varepsilon_r = 2$ which accounts for the screening introduced by the underlying frozen orbitals [66, 17]. As expected from their similar (de-)localization, the Coulomb integrals of the S and AS states are almost identical.² Besides a constant interaction charging energy U , the model defined in Eq. (22) contains exchange interaction and pair-hopping terms, both proportional to J , which are responsible for the electronic correlation. The electrostatic interaction with the substrate is known to stabilize charges on atoms and molecules [87, 65, 84] due to image charge and polaron formation. We account for this stabilization with the additional Hamiltonian $H_{\text{mol-env}} = -\delta \hat{N}^2$. The orbital energies $\varepsilon_S = -3.1$ eV and $\varepsilon_{AS} = -2.8$ eV as well as the image-charge renormalization $\delta = 0.43$ eV are obtained from the experimental resonances of the neutral molecule and previous experimental results on other molecules as detailed in the supplemental material of [22].

Many-body interaction manifests itself most strikingly for the ground state DCV5T^{2-} , which will therefore be discussed at first. Consider the two many-body states, in which the two extra electrons both occupy either the S or the AS state: They differ in energy by the energy 2Δ , where $\Delta = \varepsilon_{AS} - \varepsilon_S$ is the single-particle level spacing between the S and the AS state. These two many-body states interact via pair-hopping of strength J , leading to a level repulsion. As long as $\Delta \gg J$, this effect is negligible. In DCV5T, though, the single-particle level spacing Δ is small compared to the pair-hopping J , leading to an entangled ground state of DCV5T^{2-} as

$$|2, 0\rangle = \cos \theta \hat{d}_{S\uparrow}^\dagger \hat{d}_{S\downarrow}^\dagger |0, 0\rangle + \sin \theta \hat{d}_{AS\uparrow}^\dagger \hat{d}_{AS\downarrow}^\dagger |0, 0\rangle, \quad (23)$$

with $|N, m\rangle$ the m^{th} excited N particle state of DCV5T and $\theta = \arctan(J/\Delta)/2$. Note that here, as $J/\Delta \approx 2.6$, this state shows more than 30% contribution from both constituent states, is strongly entangled, and therefore it can not be approximated by a single Slater determinant. The first excited state of DCV5T^{2-} is a triplet with one electron in the S and one in the AS orbital at about 54 meV above the ground state, as shown in Fig. 7.

²For the Coulomb integrals we obtain $U_{S-S} = 1.37$ eV, $U_{AS-AS} = 1.43$ eV, $U_{S-AS} = 1.37$ eV.

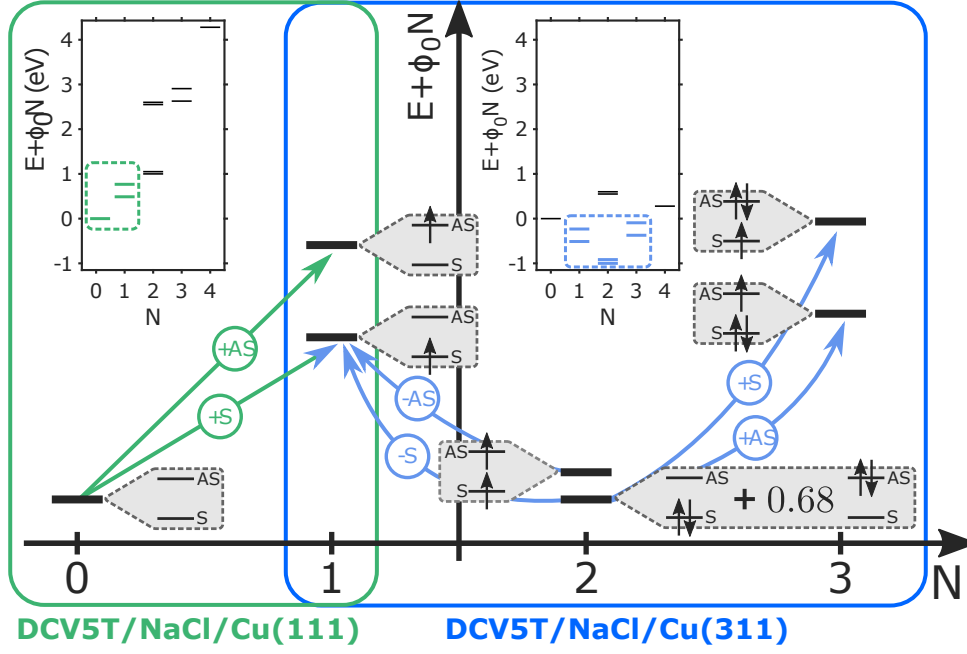


Fig. 7: Scheme of the many-body transitions associated to the measured resonances. In the green framed panel the transition between the neutral and the singly charged DCV5T⁻ are illustrated (DCV5T/NaCl/Cu(111)). In the blue framed panel the transitions involving DCV5T⁻, DCV5T²⁻ and DCV5T³⁻ are analyzed (DCV5T/NaCl/Cu(311)). The electronic structure associated to the different many-body states is explicitly given in the gray labels. In the insets, the many-body spectra of the molecule on the two corresponding substrates are plotted. From [22].

The level repulsion in DCV5T²⁻ mentioned above leads to a significant reduction of the ground state energy by roughly 0.5 eV. This effect enhances the stability of the doubly charged molecule to the disadvantage of DCV5T⁻, which has just a single extra electron and therefore does not feature many-body effects. Quantitatively, this is captured by the addition energies $E_N^{\text{add}} = E_{N+1,0} - 2E_{N,0} + E_{N-1,0}$ being a measure of the stability of the N particle ground state. Within the framework of the many-body theory, as sketched in Fig. 7, the apparent orbital reversal between Fig. 6a and Fig. 6b is naturally explained. To this end, as mentioned above, tunneling events in the STM experiments have to be considered as *transitions* between the many-body states of different charges N (see arrows in Fig. 7). The spatial fingerprints of the transitions and hence their appearance in STM images is given by the orbital occupation *difference* between the two many-body states and is indicated by the labels S and AS in Fig. 7. When on NaCl(2ML)/Cu(111), the DCV5T molecule is in its neutral ground state, see green panel in Fig. 7. A sufficiently large positive sample bias triggers transitions to the singly charged DCV5T⁻: The S and AS transitions subsequently become energetically available in the expected order of the corresponding single-particle states. A fast tunneling of the extra electron to the substrate restores the initial condition enabling a steady-state current.

When on NaCl(2ML)/Cu(311) the molecule is doubly charged and in the entangled ground state described by Eq. (23), see Fig. 7. At sufficiently high positive sample bias the transitions to DCV5T³⁻ are opening, enabling electron tunneling from the tip to the molecule. The topog-

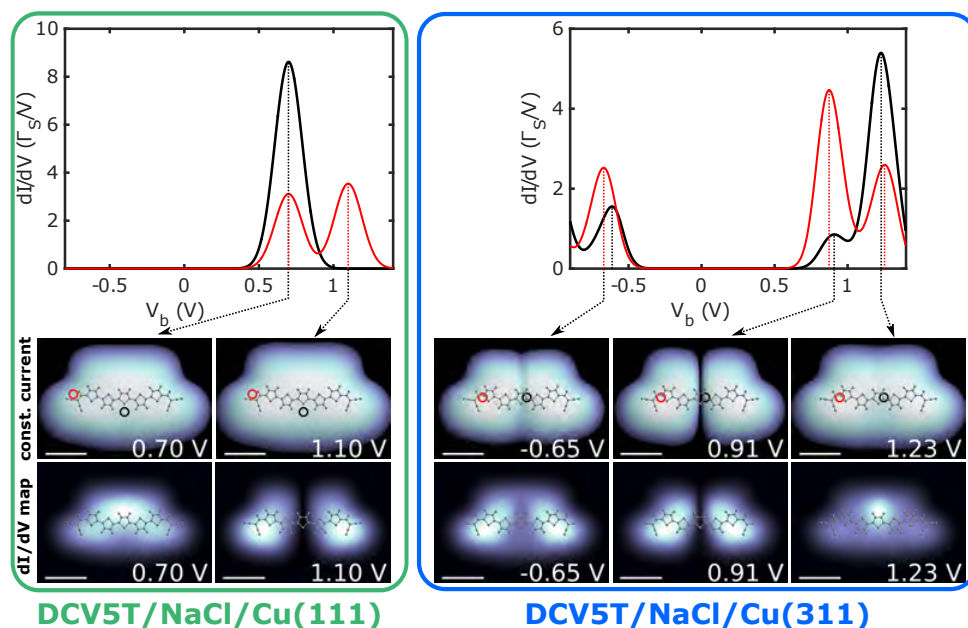


Fig. 8: Theoretical simulations of dI/dV spectra (top), constant-current STM images (center) and dI/dV maps (bottom) on the individual molecule DCV5T on NaCl/Cu(111) (a) and NaCl/Cu(311) (b) respectively. dI/dV spectra were recorded on (black) and off (red) center of the molecule as indicated by dots in the constant-current STM images. From [22].

raphy of these transitions is again obtained by comparing the 2- and the 3- (excess) electron states of DCV5T (cf. Fig. 7). The transition to the 3-particle *ground* state occurs by the population of the AS state and involves the *first* component of the entangled 2-electron ground state only. The second component cannot contribute to this transition, which is bound to involve only a *single* electron tunneling event. Correspondingly, at a larger bias the *first excited* 3-particle state becomes accessible, via a transition involving the *second* component of the 2-particle ground state only. This transition has a characteristic S state topography. Hence, although the electronic structure of the 3-electron states does follow the Aufbau principle, the entanglement of the 2-particle ground state leads to the apparent reversal of the orbital sequence.

In addition to the many-body spectrum we calculated the full dynamics of subsequent tunneling processes for all relevant situations, resulting in the calculated dI/dV characteristics, constant current maps and constant height dI/dV maps for a DCV5T single-molecule junction presented in Fig. 8. A qualitative agreement with the experimental results of Fig. 6 can be observed both for the relative strength of the spectral peaks and the dI/dV maps. The above discussed apparent orbital reversal is fully consistent with the calculations.

The experimental data of DCV5T on the Cu(311) substrate at negative bias also show a non-standard feature. The dI/dV map at resonance resembles a superposition of the S and AS orbital, see Fig. 6b. The effect is also reproduced in the theoretical simulations presented in Fig. 8. This can be rationalized in terms of a non-equilibrium dynamics associated to a population inversion predicted for Cu-Phthalocyanine [17]. The transition between the 2- and the 1-particle ground states has the topography of an S orbital. Its close vicinity to the ground state

implies that also the 2-particle first excited state should participate in transport. Moreover, the transition which connects the latter to the 1-particle ground state vanishes if the tip is in the vicinity of the molecular center, thus producing a nodal plane in the dI/dV topography and a large population of the 2-particle excited state. Though, this non-equilibrium induced population inversion is in competition with relaxation processes which conserve the molecular charge. This experiment indirectly proves that, although not negligible, this relaxation is by far not the fastest process for STM on thin insulating films: in the opposite case the nodal plane at the negative bias resonance would not have been observed.

In conclusion, we showed that a reduction of the single-particle level spacing of two frontier orbitals enables the manifestation of strong electron-correlation effects in single molecules. Here, the single-particle level spacing engineered by dicyanovinyl-substitution is leading to an apparent reversal of orbital sequence and a strongly-entangled ground state of DCV5T^{2-} . The many body description of the electronic transport is capable of reconciling the experimental observations of the orbital reversal with the fundamental oscillation theorem of quantum mechanics and shows how to achieve quantum entanglement of frontier orbitals in molecules.

5 Conclusions

The transport characteristics of correlated single-molecule junctions show a fascinating spectrum of different phenomena stemming from the interplay between the electron-electron correlation on the molecule and the tunneling coupling to the electrodes. A crucial role is played by the contacts. The control over their conformation down to atomic scale precision is often required to achieve quantitative reproducibility of the single current voltage characteristics. Scanning tunneling microscopy can achieve these standards and, with its unique capability of combining spectroscopy and topography, has proven a valuable tool to investigate correlation phenomena in single-molecule junctions. We classified the latter in extrinsic and intrinsic and concentrated on the second class, which originate directly from the entangled nature of the molecular many-body states. After introducing the Liouville approach to the transport problem, we have applied it to two examples of intrinsic correlation phenomena: the non-equilibrium spin crossover and the apparent orbital reversal. The transport characteristics were calculated for relatively simple models, based on a very small number of frontier orbitals, for which the full interaction Hamiltonian has been taken into account. In both cases, the topographical and spectral fingerprints of the correlation have been identified and criteria have been given to define the class of molecules in which similar phenomena can occur. We think that the study of correlation effects in single-molecule junctions is an open research fields with many challenges. Theoretically a unified approach to the transport problem is still lacking, while experimentally the advantages of different experimental techniques should be combined to reach a better control of the molecular many-body states and to study the signatures of their complex and fascinating dynamics.

A Derivation of the generalized master equation

The starting point is the Liouville-von Neumann equation Eq. (3), which we project on the separable and non-separable components via the operators $\mathcal{P}$ and $\mathcal{Q} = 1 - \mathcal{P}$, respectively

$$\begin{cases} \mathcal{P}\dot{\hat{\rho}} = \mathcal{P}\mathcal{L}\mathcal{P}\hat{\rho} + \mathcal{P}\mathcal{L}\mathcal{Q}\hat{\rho} \\ \mathcal{Q}\dot{\hat{\rho}} = \mathcal{Q}\mathcal{L}\mathcal{P}\hat{\rho} + \mathcal{Q}\mathcal{L}\mathcal{Q}\hat{\rho} \end{cases} \quad (24)$$

We formally solve the second equation with the help of the propagator: $\mathcal{G}_{\mathcal{Q}}(t, s) = e^{\mathcal{Q}\mathcal{L}(t-s)}$

$$\mathcal{G}_{\mathcal{Q}}(0, t) \mathcal{Q}\dot{\hat{\rho}} - \mathcal{G}_{\mathcal{Q}}(0, t) \mathcal{Q}\mathcal{L}\mathcal{Q}\hat{\rho} = \frac{d}{dt} [\mathcal{G}_{\mathcal{Q}}(0, t) \mathcal{Q}\hat{\rho}] = \mathcal{G}_{\mathcal{Q}}(0, t) \mathcal{Q}\mathcal{L}\mathcal{P}\hat{\rho},$$

which, by integration implies

$$\mathcal{G}_{\mathcal{Q}}(0, t) \mathcal{Q}\dot{\hat{\rho}} - \mathcal{Q}\hat{\rho}(0) = \int_0^t \mathcal{G}_{\mathcal{Q}}(0, s) \mathcal{Q}\mathcal{L}\mathcal{P}\hat{\rho}(s) ds$$

and, by multiplication on the left by $\mathcal{G}_{\mathcal{Q}}(t, 0)$

$$\mathcal{Q}\hat{\rho}(t) = \mathcal{G}_{\mathcal{Q}}(t, 0) \mathcal{Q}\hat{\rho}(0) + \int_0^t \mathcal{G}_{\mathcal{Q}}(t, s) \mathcal{Q}\mathcal{L}\mathcal{P}\hat{\rho}(s) ds. \quad (25)$$

We now insert (25) into the first of Eq. (24) taking a separable initial condition $\hat{\rho}(0) = \hat{\rho}_{\text{mol}}(0) \otimes \hat{\rho}_{\text{leads}}$, which implies $\mathcal{Q}\hat{\rho}(0) = 0$. Further, the following relations follow from the definition of $\mathcal{P}$ and the fact that the tunneling Hamiltonian does not conserve the lead particle number

$$\mathcal{P}\mathcal{L}_{\text{tun}}\mathcal{P} = 0, \quad [\mathcal{P}, \mathcal{L}_{\text{mol}}] = [\mathcal{P}, \mathcal{L}_{\text{leads}}] = \mathcal{P}\mathcal{L}_{\text{leads}} = 0. \quad (26)$$

With all these observations, we can write the closed integro-differential equation for $\mathcal{P}\hat{\rho}$

$$\mathcal{P}\dot{\hat{\rho}}(t) = \mathcal{L}_{\text{mol}}\mathcal{P}\hat{\rho}(t) + \int_0^t \mathcal{P}\mathcal{L}\mathcal{G}_{\mathcal{Q}}(t, s) \mathcal{Q}\mathcal{L}\mathcal{P}\hat{\rho}(s) ds, \quad (27)$$

from which we can already identify (remember that $\mathcal{P}^2 = \mathcal{P}$) a propagator kernel of the form

$$\mathcal{K}(t-s) = \mathcal{P}\mathcal{L}e^{\mathcal{Q}\mathcal{L}(t-s)}\mathcal{Q}\mathcal{L}\mathcal{P}.$$

We further manipulate the expression above with the idea of better emphasizing the perturbative expansion in $\mathcal{L}_{\text{tun}}$. By expanding the exponential, we obtain

$$\mathcal{P}\mathcal{L}e^{\mathcal{Q}\mathcal{L}t}\mathcal{Q}\mathcal{L}\mathcal{P} = \sum_{n=0}^{\infty} \frac{1}{n!} \mathcal{P}\mathcal{L}\mathcal{Q}(\mathcal{Q}\mathcal{L}\mathcal{Q})^n \mathcal{Q}\mathcal{L}\mathcal{P}t^n$$

On the other hand, with the help of the relations among Liouvillian and projectors (26) one easily obtains

$$\mathcal{P}\mathcal{L}\mathcal{Q} = \mathcal{P}\mathcal{L}_{\text{tun}}, \quad \mathcal{Q}\mathcal{L}\mathcal{P} = \mathcal{L}_{\text{tun}}\mathcal{P}, \quad \mathcal{Q}\mathcal{L}\mathcal{Q} = \mathcal{Q}(\mathcal{L}_{\text{mol}} + \mathcal{L}_{\text{leads}} + \mathcal{Q}\mathcal{L}_{\text{tun}}\mathcal{Q}).$$

Since it is also clear, from the definition of $\mathcal{Q}$ that $[\mathcal{Q}, \mathcal{Q}\mathcal{L}_{\text{tun}}\mathcal{Q}] = 0$ we can write

$$\mathcal{K}(t) = \sum_{n=0}^{\infty} \frac{1}{n!} \mathcal{P}\mathcal{L}_{\text{tun}}\mathcal{Q}(\mathcal{L}_{\text{mol}} + \mathcal{L}_{\text{leads}} + \mathcal{Q}\mathcal{L}_{\text{tun}}\mathcal{Q})^n t^n \mathcal{L}_{\text{tun}}\mathcal{P} \quad (28)$$

where, according to Eq. (26), the first $\mathcal{Q}$ projector from the left can be omitted and, by resumming the series, one obtains the desired result of Eq. (7).

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