Cotunneling theory of inelastic STM spin spectroscopy

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We propose cotunneling as the microscopic mechanism that makes possible inelastic electron spectroscopy of magnetic systems in surfaces for a wide range of systems, including single magnetic adatoms, molecules and molecular stacks. We describe electronic transport between the scanning tip and the conducting surface through the magnetic system (MS) with a generalized Anderson model, without making use of effective spin models. Transport and spin dynamics are described with an effective cotunneling Hamiltonian in which the correlations in the magnetic system are calculated exactly and the coupling to the electrodes is included up to second order in the tip-MS and MS-substrate. In the adequate limit our approach is equivalent to the phenomenological Kondo exchange model that successfully describe the experiments. We apply our method to study in detail inelastic transport in two systems, stacks of Cobalt Phthalocyanines and a single Mn atom on Cu$_2$N. Our method accounts both, for the large contribution of the inelastic spin exchange events to the conductance and the observed conductance asymmetry.

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I. INTRODUCTION

The combination of two powerful techniques, Inelastic Electron Tunneling spectroscopy (IETS) and Scanning Tunneling Microscope (STM) makes it possible to probe inelastic excitations with subatomic resolution. The STM-IETS technique was first applied to the study of vibrational excitations of single molecules on surfaces, and has more recently been used to study spin excitations of a single and a few magnetic atoms and molecules deposited on surfaces. In STM-IETS, electrons tunnel between the tip and the conducting substrate going through the magnetic system. As the bias voltage $V$ is increased, a new conduction channel opens whenever $eV$ is larger than the energy of some internal excitation of the atom, which results in a stepwise increase of the differential conductance $dI/dV$ and a peak or dip in the $d^2I/dV^2$. Tracing the evolution of the elementary excitations as a function of an applied magnetic field and fitting to effective spin Hamiltonians permits to infer the single ion magnetic anisotropy tensor as well as exchange coupling between adjacent atoms and molecules.

The IETS-STM technique has been applied to a variety of magnetic systems weakly coupled to a conducting substrate. The list includes a single transition metal atom (Mn, Fe, Co) deposited on a single monolayer of Cu$_2$N on Copper, to chains of up to 10 Mn atoms on the same substrate, to Fe-phthalocyanine (Fe-PC) molecules on oxidized Cu$_2$N, to stacks of Co-PC molecules on Pt, to Mn-PC on PbO$_2$, and, more recently, a single Fe atom on InSb, a semiconducting substrate. For all these systems it is possible to describe the spin exchange assisted tunneling, which accounts for the coupling between transport electrons and the localized spins of the magnetic atoms or molecules, with Kondo-like Hamiltonians. Whereas this approach successfully describes the main experimental results, including the differential conductance, as well as effects related to current driven spin dynamics and/or spin polarized tip, there are questions that can not be addressed using effective spin models:

1. Why the spin assisted inelastic conductance is comparable to the elastic contribution, in contrast with the phonon-assisted inelastic contribution?

2. What is the microscopic origin of the spin exchange tunneling?

3. Why the inelastic conductance is not always symmetric with respect to the inversion of the bias polarity?

In this work we provide a theoretical framework to model the existing STM-IETS experiments that addresses these questions. Our starting point is a generalized multi-orbital/multi-site Anderson model, in which the electrons in the localized orbitals of the magnetic system (MS) are hybridized to the itinerant states of the tip and the surface. The states of the MS are calculated by exact diagonalization of a microscopic Hamiltonian that can include Coulomb repulsion, crystal field and spin-orbit coupling. Transport and spin dynamics are described by means of an effective cotunneling Hamiltonian in which the coupling to the tip and surface is included up to second order. This approach works provided that the charging energy of the MS is much larger than the temperature, applied bias potential and the electrode induced broadening of the MS levels. Thus, the MS must be in the Coulomb Blockade situation, where the charge is a good quantum number and current flows due to quantum charge fluctuations, known as cotunneling.

When applied to a single orbital Anderson model, the effective cotunneling Hamiltonian that we obtain is identical to the Kondo model obtained through the standard Schrieffer-Wolff transformation. Our method can applied to systems with more than one localized orbital, necessary to address most experimentally relevant systems. The effective cotunneling Hamiltonian...
describes transitions between the different many-body states of the MS induced by their coupling to the itinerant electrons. This permits to calculate the scattering rates, both for the dissipative dynamics of the spin excitations of the MS coupled to the leads and those leading to the current.

The rest of the paper is organized as follows. In Sec. II we present the derivation of the effective Hamiltonian and the procedure used to calculate the current, leaving some of the technical details for the appendix. In Sec. III we apply our approach to the case of a single site Anderson model, which permits to test our approach against well established results. In Sec. IV we implement our approach to model transport through stacks of CoPc molecules. For that matter, we describe the CoPc stacks by means of a Hubbard model. In Sec. V we study the case of a single Mn adatom on a Cu$_2$N surface using a multi-orbital Anderson model where Coulomb interaction, crystal field and spin-orbit coupling in the MS are included in the Hamiltonian and treated exactly, by means of numerical diagonalization. In section VI we summarize our main results.

II. THEORY

A. Effective Hamiltonian

We describe a magnetic system weakly coupled to two electrodes, denoted as tip (T) and surface (S) without loss of generality, using the following Hamiltonian:

$$\mathcal{H} = \mathcal{H}_T + \mathcal{H}_S + \mathcal{H}_{MS} + \mathcal{V}_{\text{tun}}.$$  (1)

Here $\mathcal{H}_T + \mathcal{H}_S$ correspond to the Hamiltonian of the two electrodes, $\mathcal{H}_{MS}$ the magnetic system and $\mathcal{V}_{\text{tun}}$ the tunneling Hamiltonian. We shall consider the two electrodes as free electron reservoirs, i.e., $\mathcal{H}_T + \mathcal{H}_S = \sum_{\alpha} \epsilon_\alpha f^\dagger_{\alpha} f_{\alpha}$, where $f^\dagger_{\alpha}$ ($f_{\alpha}$) is the creation (annihilation) operator of a quasiparticle with single particle number $\alpha \equiv \{k, \eta, \sigma\}$, with momentum $k$, electrode $\eta = T, S$ and spin projection in the quantization direction $\sigma$. In general, the central region has a complicated many-body Hamiltonian that includes Coulomb repulsion, spin-orbit coupling, crystal field terms and so on. The many-body eigenstates of $\mathcal{H}_{MS}$, $|q, n\rangle$ have a well defined number of electrons $q$. Only 3 charge sectors, $q = q_0, +$ and $-$, are relevant. The $q_0$ corresponds to the ground state of the MS. The sectors $+$ and $-$ correspond to the MS with an extra electron ($q_0 + 1$) and an extra hole ($q_0 - 1$) respectively. The Hamiltonian of the isolated MS can be written as:

$$\mathcal{H}_{MS} = \sum_{q,n} E_q,n |q, n\rangle \langle q, n|.$$  (2)

The tunneling Hamiltonian is given by

$$\mathcal{V}_{\text{tun}} = \sum_{i,\alpha} V_{\alpha,i} f^\dagger_{\alpha} d_i + h.c. = \hat{\mathcal{V}}^- + \hat{\mathcal{V}}^+,$$  (3)

where the tunneling of electrons in and out the MS are described by $\hat{\mathcal{V}}^+$ and $\hat{\mathcal{V}}^-$ respectively. Here $d_i^\dagger$ ($d_i$) are the creation (annihilation) operator of an electron in a single particle state $i \equiv \{i, \sigma\}$ with orbital quantum numbers $i$ and spin $\sigma$. We assume that single-particle tunneling events are spin conserving and spin independent, i.e., $V_{k\eta, i\sigma'} = V_{k\eta, i\sigma}$. We will start with the uncoupled Hamiltonian $\mathcal{H}_0 = \mathcal{H}_T + \mathcal{H}_S + \mathcal{H}_{MS}$. Since $\mathcal{H}_0$ commutes with the charge operator of the MS, the eigenstates of $\mathcal{H}_0$ can be labeled according to the charge $q$ in the central atom. We assume that the eigenvalues in the $q_0$ sector are separated by a large gap from the states in the $q = \pm$ sectors, see Fig. 1. In particular, the chemical potentials of the MS, defined as $\mu_{\pm} = E_G(N_{\text{e}}) - E_G(N_{\text{e}} - 1)$ and $\mu_\text{c} = E_G(N_{\text{e}} + 1) - E_G(N_{\text{e}})$, with $E_G(N_{\text{e}})$ the ground state energy corresponding to $N_{\text{e}}$ electrons, must satisfy $|\mu_{\text{h}} - \mu_{\text{c}}|, |\mu_\text{c} - \mu_{\text{h}}| \gg k_\text{B}T, |eV|$. This corresponds to the conditions of deep cotunneling in which the sequential-first order transitions are exponentially suppressed. In this limit we can use degenerate perturbation theory to determine the dynamics of the states in the $q_0$ sector, which we denote with $|N\rangle$. These states are tensor products of the electrode ground states and the many body states $|q, n\rangle$ of the magnetic system. The tunneling operator connects them to states $|M_{\pm}\rangle$ that are products of electrode states with 1 quasiparticle and MS states $|q_0 \pm 1, m\rangle$. Unless otherwise stated, in the rest of the paper we label the MS islands states with the shorthand notation $|n\rangle \equiv |q_0, n\rangle$ and $|m_{\pm}\rangle \equiv |q_0 \pm 1, m\rangle$.

Using degenerate perturbation theory we can obtain...
an effective Hamiltonian for the \( q_0 \) sector where the tunneling events are included to the lowest order:

\[
\mathcal{H}_{\text{cotun}} = \sum_{M\mp} \frac{\mathcal{V}_{\pm} |M\mp \rangle \langle M\mp| \mathcal{V}_{\pm}}{E_{M\mp} - E_0}.
\]  

(4)

In the calculation of the effective Hamiltonian we are neglecting the energy variations of the unperturbed states inside the \( q_0 \) manifold, all taken to be \( E_0 \), compared to the charging energy. When expanding this operator in the basis of the electrode quasiparticles and the MS many-body states, we can write the effective Hamiltonian for the \( q_0 \) sector as (see Appendix A for details):

\[
\mathcal{H}_{\text{cotun}} = \sum_{\alpha,\alpha'} \left[ \hat{O}^{\mp}_{\alpha\alpha'} - \hat{O}^{\mp}_{\alpha'\alpha} \right] f_{\alpha} f_{\alpha'} + \sum_{\alpha} T^{\mp}_{\alpha\alpha},
\]  

(5)

where

\[
\hat{O}^{\pm}_{\alpha\alpha'} \equiv \sum_{n,n'} \langle n | \hat{O}^{\pm}_{\alpha\alpha'} | n' \rangle | n \rangle \langle n' |.
\]  

(6)

are operators that act exclusively on the subspace \( |q_0, n \rangle \) of the neutral MS. Their matrix elements read:

\[
\langle n | \hat{O}^{\mp}_{\alpha\alpha'} | n' \rangle = \sum_{i'i',\sigma',\sigma} \frac{V_{\alpha,i} V_{\alpha',i'}^{*}}{E_{i'\mp} - E_0 - \epsilon_{\alpha'}} \gamma_{n,n'}^{m_{\mp}}(i'i',\sigma,\sigma'),
\]  

(7)

and

\[
\langle n | \hat{O}^{\mp}_{\alpha\alpha'} | n' \rangle = \sum_{i'i',\sigma',\sigma} \frac{V_{\alpha,i} V_{\alpha',i'}^{*}}{E_{i'\pm} - E_0 + \epsilon_{\alpha'}} \gamma_{n,n'}^{m_{\pm}}(i'i',\sigma,\sigma'),
\]  

(8)

where

\[
\gamma_{n,n'}^{m_{\mp}}(i'i',\sigma,\sigma') = \langle n | d_{\sigma} m_{\mp} | i'i' \rangle \langle i'i' | d_{\sigma'} m_{\pm} | n' \rangle.
\]  

(9)

Eqs. (5)-(8) constitute the cornerstone of the formalism. The Hamiltonian \( \mathcal{H}_{\text{cotun}} \) in Eq. (5) describes the scattering of a quasiparticle from the single particle state \( \alpha' \) to \( \alpha \) in the electrodes together with a transition between two many-body states of the MS within the \( q_0 \) manifold. Three types of elementary processes are described by the effective cotunneling Hamiltonian: elastic processes in which transport electrons are transferred between both electrodes without changes in the central region, creation of electron-hole pair in a given electrode with the corresponding transition in the central island, and inelastic tunneling events. In all of them, it is apparent from Eqs. (9) and (10) that the excitations within the \( q_0 \) manifold in the MS occurs via virtual transitions to the charged manifolds \( q = - \) and \( q = + \). An scheme of each of these processes can be seen in Fig. 1.

Very much like in the case of effective Kondo models, the quasiparticle scattering events can be classified in four groups depending on whether they include, or not, spin flip and/or electrode transition. In turn, the spin conserving events are split in two more groups, depending on weather or not they have spin dependent amplitudes. Because of the spin rotational invariance imposed in the tunneling Hamiltonian \( \mathcal{H}_{\text{cotun}} \), quasiparticle spin flip events imply spin transfer to the MS. Finally, the last term in Eq. (5) describes a renormalization of the many-body levels of the MS and can be re-adsorbed into a new Hamiltonian for the central part, \( \mathcal{H}_{\text{MS}} = \mathcal{H}_{\text{MS}} + \sum_{\alpha} T^{\mp}_{\alpha\alpha} \), so it will be omitted in the following analysis.

For a fixed set of initial and final quasiparticle states, \( \alpha, \alpha' \), the matrices (7-8) have, at most, the dimension of the \( q_0 \) manifold. For instance, as discussed in detail in Sec. III in so called Anderson model, when the states with \( q = q_0 \) in the island are those of an unpaired electron, the dimension of the matrices (7-8) is 2, corresponding to the two spin projections of a spin 1/2. As a result, the Hamiltonian (5) describes a Kondo coupling between the electrode and the spin 1/2 of the MS.

**B. Master equation, transition rates and current**

The procedure described above yields an effective Hamiltonian of the MS coupled to the electrodes for which the states of the \( q = \pm \) sectors have been integrated out. The effective total Hamiltonian of the electrodes coupled to the \( q_0 \) manifold reads:

\[
\mathcal{H}_{\text{eff}} = \sum_{n} E_{n} |n\rangle \langle n| + \mathcal{H}_{T} + \mathcal{H}_{S} + \mathcal{H}_{\text{cotun}}.
\]  

(11)

This Hamiltonian serves as starting point to calculate both current and dynamics of the many body states of the MS within the \( q_0 \) manifold. The dissipative dynamics of the \( n \) states in the MS is induced by the coupling to the electrodes as described by \( \mathcal{H}_{\text{cotun}} \). The master equation for the populations of the MS states, \( P_n \), is given by

\[
\frac{dP_n}{dt} = \sum_{n'} W_{n,n'} P_{n'} - P_n \sum_{n'} W_{n,n'},
\]  

(12)

where the transition rates \( W_{n,n'} \) for the MS to go from state \( n \) to \( n' \) due to quasiparticle scattering in the electrodes are calculated by applying the Fermi Golden Rule with the perturbation given by the tunneling Hamiltonian (5). The steady state solutions of this master equation depend, in general, on the Hamiltonian parameters, the temperature and the bias voltage. At zero bias, the steady state solutions are those of thermal equilibrium. At finite bias, \( P_n (V) \) can depart significantly from equilibrium depending on the relative efficiency of the transport assisted excitations and relaxations.

The rates \( W_{n,n'} \) are the sum of scattering processes in which the initial and final electrode and spin quantum numbers of the quasiparticle are well defined,

\[
W_{n,n'} = \sum_{\sigma' \sigma} W_{n,n'}^{\sigma \sigma' n'}.
\]  

(13)
An explicit expression for the spin and electrode dependent scattering rate $W_{nn',nn''}^{\eta\eta'}$ is given in the Appendix A Eq. (11). The expression involves a convolution over the energy dependent density of states and effective cotunneling rates. A simpler expression is obtained by doing a number of approximations in Appendix B, as explained in Appendix B. First, we assume that the electrodes have a flat density of states within a bandwidth larger than all relevant energy scales in the problem: temperature, bias and the excitations energies of the MS within the $q_0$ manifold. Second, we neglect the energy dependence of the hopping matrix elements $V_{nn'}^{\eta\eta'} = V_{nn'}^{\eta\eta'}$. These approximations are justified in IETS experiments where the temperature is at most a few Kelvins and the applied bias is below 50 mV. If we introduce the excitation energy associated to the transition between $n'$ and $n$ states in the $q_0$ manifold, $\Delta_{nn'} = E_n - E_{n'}$ and we define the average energy $\bar{\varepsilon}_{nn'}^{\eta\eta'} = 1/2(\varepsilon_n + \varepsilon_{n'} + \Delta_{nn'})$, the transition rates $W_{nn'}^{\eta\eta'}$ obtained in Appendix B can be expressed as

$$W_{nn'}^{\eta\eta'} \approx \sum_{\sigma\sigma'} \frac{2\pi \rho_{\eta\sigma} \rho_{\eta'\sigma'}}{\hbar} G(\mu_{\eta} - \mu_{\eta'} + \Delta_{nn'}) \Sigma_{nn'}^{\eta\eta'}(\bar{\varepsilon}_{nn'}^{\eta\eta'}) \label{eq:14}$$

where $G(\omega) = \frac{1}{1 - \exp[-\beta \omega]}$ and $\rho_{\eta\sigma}$ are the spin and electrode resolved density of states. The many-body matrix elements $\Sigma_{nn'}^{\eta\eta'}(\bar{\varepsilon})$ are given by

$$\Sigma_{nn'}^{\eta\eta'}(\bar{\varepsilon}) = |n\rangle \left( \hat{O}_{\eta\eta'}^{(+)}(k) \hat{\kappa}_{\eta'\eta} - \hat{O}_{\eta'\eta}^{(-)}(k) \hat{\kappa}_{\eta'\eta} \right) |n'\rangle |^2 \label{eq:15}$$

where $\kappa \equiv k(\bar{\varepsilon})$, i.e., the quasiparticle energy that appear in the denominators are replaced by the corresponding bias-dependent average energy $\bar{\varepsilon}_{nn'}^{\eta\eta'}$.

In this context, the current is given by\textsuperscript{18,22}

$$I_{T \rightarrow S} = e \sum_{n,n'} P_n(V) \left( W_{nn',nn'}^{S \rightarrow T} - W_{nn',nn'}^{T \rightarrow S} \right) \label{eq:16}$$

where $e$ is the (negative) electron charge. This equation has a physically transparent meaning: the current is proportional to the transition rates of quasiparticles changing electrode. These rates involve transitions of the MS from the state $n$, which is occupied with probability $P_n(V)$, to state $n'$, including elastic events $n = n'$.

Our convention for the applied bias is such that $eV = \mu_S - \mu_T$ (electrons move from tip to surface for a positive applied bias). The bias implies a small charge accumulation both in the tip and the surface which in turn involves a shift of their chemical potentials with respect to their equilibrium value, denoted by $E_F$. Without loss of generality we can write $\mu_S = E_F + xeV$, $\mu_T = E_F + (x-1)eV$, where $x$ is an undetermined parameter that relates the bias voltage to the shift of the chemical potential in each electrode. Given the fact that the capacitance of the surface is much larger than that of the tip, it is reasonable to take $x = 0$. As we show below, this assumption makes it possible to account for the conductance asymmetry reported experimentally\textsuperscript{19,20}.

In the following, we shall express the differential conductance in units of

$$g_0 = \frac{G_0}{2} \rho_S \rho_T \left( J_{TS}^2 + W_{TS} \right), \label{eq:17}$$

where $G_0 = 2e^2/h$ is the quantum of conductance, $\rho_{\eta} = \sum_{\sigma} \rho_{\eta\sigma}$ and $J_{TS}$ and $W_{TS}$ are just the generalizations of the (momentum independent) exchange and direct coupling respectively that appears in the Anderson model, as it will be shown bellow:

$$J_{TS} = 2V_S^{(M)} V_T^{(M)} \left[ (\mu_e - E_F)^{-1} + (E_F - \mu_h)^{-1} \right], \label{eq:18}$$

and

$$W_{TS} = V_S^{(M)} V_T^{(M)} / 2 \left[ (\mu_e - E_F)^{-1} - (E_F - \mu_h)^{-1} \right] \label{eq:19}$$

where $V_{\eta}^{(M)}$ is the maximum value of the couplings between electrode $\eta$ and the orbitals of the MS.

### C. Summary of the method

The approach described above can be implemented in a wide range of situations following a sequence of well defined steps:

1. Diagonalization of the MS Hamiltonian in the 3 relevant charge sectors, $q = q_0 - 1$, $q_0$, $q_0 + 1$, providing $(q, n)$ and $E_{q,n}$.

2. Computation of the matrix elements (7) and (8) of the effective tunneling Hamiltonian operator, which requires the calculation of the many body matrix elements $\gamma$ (Eqs. (9) and (10) ) and the $\mathcal{O}$-matrix prefactors.

3. Calculation of the scattering rates (14), which depend on bias, temperature, MS-electrode coupling, electrode density of states and MS wave functions.

4. Finding the non-equilibrium steady state solutions $P_n(V)$ of the master equation (12).

5. Evaluation of the current using Eq. (10).

### D. Comparison with other cotunneling theories

The calculation of cotunneling current has been widely studied before, using different methodologies, mainly in the context of quantum dot\textsuperscript{23,24,25} and, more recently, molecules\textsuperscript{26,27}. For instance, in Ref. 34 they compute the cotunneling scattering rates by truncating the T-matrix down to second order in the electrode coupling. On the other hand, a more formal and accurate treatment, valid also in the strong-coupling regime, was introduced in Ref. 28 where the non-equilibrium Keldysh Green function formalism was used to study the inelastic spectroscopy of single adsorbed molecules.
Whereas there current obtained using these different methods is the same, our approach permits to derive an effective Hamiltonian which, in the adequate limit, is the same than the effective Kondo Hamiltonian used extensively in previous works. An interesting work addressing the relation between multiple-impurity Anderson model at half-filling and a Kondo model was presented in Ref. [34], where authors proved that a Hubbard chain of $N$ impurities coupled in parallel can be described with a $S = N/2$ $SU(2)$ spin Kondo model. In Ref. [30], authors used the same generalized Schrieffer-Wolff transformation to relate a singlet-triplet Anderson impurity with a spin model close to its quantum phase transition.

Our approach, based on an effective cotunneling Hamiltonian directly obtained from the exact description of the magnetic system, provides a microscopic justification of earlier phenomenological works, at the time that it keeps the simplicity that allows to calculate the current as described above.

III. SINGLE ORBITAL ANDERSON MODEL

In this section we revisit the very well known Anderson model for which the MS is a single site Hubbard model:

\[
H_{\text{MS}} = E_d \sum_{\sigma} d_{\sigma}^\dagger d_{\sigma} + U n_{\uparrow} n_{\downarrow},
\]

where $E_d$ is the on-site energy level, $U$ the on-site Coulomb repulsion and $n_{\sigma} = d_{\sigma}^\dagger d_{\sigma}$. We now derive an effective cotunneling Hamiltonian which, as we show below, turns out to be identical to the spin $1/2$ Kondo model by means of a Schrieffer-Wolff transformation. By so doing, we test the validity of our approach and shed some light on the origin of the large contribution of the inelastic spin assisted tunneling to the conductance. The single-site Hubbard Hamiltonian has only 3 possible charge states, empty, singly and doubly occupied. The singly occupied manifold has two states, $|\uparrow\rangle$ and $|\downarrow\rangle$ with energy $E_d$. The empty and doubly occupied manifolds have only 1 state each, $|\uparrow\downarrow\rangle$ with energy $2E_d + U$ for the + manifold and $|\downarrow\downarrow\rangle$ with energy 0 for the − manifold respectively. If $E_d + U > E_F > E_d > k_B T$ the ground state has $q_0 = 1$ and classical charge fluctuations are frozen. Hence, the virtual transition operators acting on the $q_0 = 1$ space have dimension two and can be expressed as Pauli matrices, acting on the spin space.

After a straightforward calculation we find the effective cotunneling Hamiltonian with 3 contributions. First, the famous exchange assisted Kondo term

\[
H_{\text{cot},1} = \sum_{kk',\eta\eta',\sigma\sigma'} J_{kk',\eta\eta',\sigma\sigma'} \hat{S}_{\sigma\sigma'}^\dagger f_{k\eta}\sigma^\dagger f_{k'\eta'}\sigma',
\]

with

\[
J_{kk',\eta\eta'} = V_{k\eta} V_{k'\eta'} \left[ \frac{1}{E_d + U - \epsilon_{k\eta}} + \frac{1}{\epsilon_{k'\eta'} - E_d} \right].
\]

The second term $H_2 = \sum_{kk',\eta\eta',\sigma\sigma'} \mathcal{H}_2(kk',\eta\eta',\sigma)$ in the Hamiltonian corresponds to a direct (spin-independent) interaction, also obtained in the Schrieffer-Wolff transformation

\[
H_{\text{cot},2} = \sum_{kk',\eta\eta',\sigma} W_{kk',\eta\eta'} f_{k\eta}\sigma^\dagger f_{k'\eta'}\sigma,
\]

where

\[
W_{kk',\eta\eta'} = V_{k\eta} V_{k'\eta'} \left[ \frac{1}{E_d + U - \epsilon_{k\eta}} - \frac{1}{\epsilon_{k'\eta'} - E_d} \right].
\]

Notice how in this model, the exchange assisted $J_{kk',\eta\eta'}$ and the direct tunneling term $W_{kk',\eta\eta'}$ have a common origin, namely, virtual charging of the magnetic site. Importantly, we see how we can have the spin-flip term much larger than the direct term. In particular, in the so called symmetric case, for which $E_d + U - E_F = E_F - E_d$, the direct term vanishes altogether, due to a cancellation between the electron addition and hole addition channels. In that situation only the spin-flip assisted tunneling would be possible. Thus, the cotunneling picture provides a natural scenario for the large contribution of the inelastic contribution to the conductance. Finally, a third term $H_3 = \sum_{k,\eta,\sigma} \mathcal{H}_3(k,\eta,\sigma)$ is obtained, which can be considered as a renormalization of the on-site energy level.

IV. STACKS OF CoPc MOLECULES

In this section we model the IETS experiments of stacks of Cobalt phthalocyanine molecules (CoPc) deposited on Pb(111). CoPc molecules are planar molecules with $D_{4h}$ symmetry and a single Cobalt (Co) atom at its center, surrounded by four Nitrogen neighbors and enclosed by aromatic macrorcycles. A single CoPc has a ground state with spin $S = 1/2$, corresponding to an unpaired electron presumably in the $d_{z^2}$ orbital of Co. In a stack with $N + 1$ CoPc molecules, the CoPc in contact with the Pb surface acts as a dead layer that isolates the remaining $N$ molecules.

The stacking seems to be such that Cobalt atoms are underneath Nitrogen atoms of the adjacent molecule. The IETS results of stacks with $N$ active CoPc ($N+1$ molecules in total) can be interpreted as if the molecules are coupled via an antiferromagnetic coupling, which presumably comes from super-exchange between two Cobalt coupled to a common Nitrogen. The observed spin-flip excitations were successfully described using a Heisenberg model with an antiferromagnetic (AF) coupling $J \approx 18$meV.

Whereas the Heisenberg model accounts for the observed excitation energies, it can not account for either the transport mechanism or the fact that the conductance in this system is very asymmetric. In particular, some inelastic steps seen at a given bias polarity are not
seen when bias sign is reversed. Additional experiments where the charge state of the molecular stack was controlled using the STM tip as a local gate make it necessary to go beyond spin-only models.\textsuperscript{10} The observed excitation energies could be accounted for using a Hubbard model, rather than a Heisenberg model:

\[
\mathcal{H}_{\text{MS}} = E_d \sum_{i,\sigma} d_{i\sigma}^\dagger d_{i\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} + t \sum_{i,\sigma} \left( d_{i\sigma}^\dagger d_{i+1\sigma} + \text{h.c.} \right)
\]

(25)

Here \(E_d\) stands for the energy of the \(d_{z^2-r^2}\) orbital with respect to the Fermi energy, that we take at 0, \(U\) stands for the on-site Coulomb repulsion and \(t\) for the Co-Co hopping, which actually occurs through the common Nitrogen neighbor. In the strongly insulating limit, \(U \gg t\) and at half-filling (1 unpaired electron per Cobalt atom), the Hubbard model has the same low energy excitation spectra than the Heisenberg model with \(J = \frac{4t^2}{U}\). Away from half-filling, when the molecular stack is charged, the mapping to the Heisenberg model is no longer possible but still the excitation energies observed experimentally are accounted for by the Hubbard model.\textsuperscript{10} Here we focus on the half-filling case and we apply our formalism to short Hubbard chains with \(N = 2, 3, 4\) sites. We take \(U = 1.5\text{eV}\) which imposes \(t = 82\text{meV} (J \approx 18\text{meV})\), in accordance with the experimentally observed value.\textsuperscript{8,10}

\section*{A. The dimer}

The eigenvalues and eigenvectors of the Hubbard dimer can be found analytically, both for the half-filling sector and the two sectors with 1 and 3 electrons. At half filling (\(q = q_0\)) the ground state corresponds to a spin singlet, \(S = 0\), while the first excited state corresponds to a spin triplet, \(S = 1\) with excitation energy \(J\) neglecting terms of order \(t^4/U^3\), see Fig. 2(b) (in agreement with the experimental results).\textsuperscript{8,10} Referred to half-filling, the electron addition and hole addition energies are \(E_d + U\) and \(-E_d\), respectively. Thus, for the MS to be at half filling we must have \(E_d < 0\) and \(|E_d| < U\). The states of the \(q = \pm 1\) correspond to those of a single electron and a single hole, respectively.

In order to assess the effect of the relative weight of the cotunneling mediated by virtual hole and virtual electron addition (\(q_{\pm}\) channels), we have calculated \(dI/dV\) spectra obtained for the Hubbard dimer for three different values of the on-site energy \(E_d\): \(E_d = -U/2\), the so called electron hole symmetry point, \(E_d = -0.35\text{eV}\) for which virtual transitions to the \(q_{-}\) manifold are favored and \(E_d = -1.3\text{eV}\), which favors virtual transitions to the \(q_{+}\) manifold, see Fig. 1(c). Whereas the excitation step at \(\pm eV = J\) is present in all of them, both the magnitude and the bias dependence of the elastic contribution depends a lot on \(E_d\). At the electron-hole symmetry point (EHSP), the elastic conductance is zero, as in the Anderson model, and the non-monotonic lineshape right above the inelastic step is due to the depletion of the occupation of the ground state in favor of the excited state, a non-equilibrium effect discussed in our previous work.\textsuperscript{22} Both the elastic and the inelastic contributions increase when \(E_d\) is taken away from the EHSP.

When \(E_d = -1.3\text{eV}\), the virtual transition to the \(q_{+}\) manifold is dominant and cotunneling is mediated by the addition of an electron. As we mentioned in Sec. 1113 our bias convention is such that positive bias \(V\) results in an increment of the tip chemical potential with respect to the molecules and the surface. Thus, for \(V > 0\) it becomes easier to add an electron to the system, increasing the global conductance. For \(V < 0\), instead, the chemical potential of the tip is decreased, making it relatively harder to charge the dimer with an electron and reducing the cotunneling conductance thereby. In the case of \(E_d = -0.35\text{eV}\) the situation is reversed. The virtual transition to the \(q_{-}\) manifold is dominant, i.e., cotunneling is mediated by the addition of a hole (or the removal of an electron). In this case a positive bias makes it harder for the electron to tunnel out of the system, decreasing the conductance. Thus, in our calculation the asymmetry of the conductance comes from the assumption that the bias shifts mostly the tip chemical potential, and not the surface, and the fact that one of the two cotunneling channels (virtual addition of either an electron or a hole) is dominant. Comparing with the experimental results\textsuperscript{8} we infer that the double CoPc molecule system is close to the electron addition point. This has been further confirmed by additional experiments by the same group.\textsuperscript{10}
B. The trimer and the tetramer

We now consider the Hubbard chains with either $N = 3$ and $N = 4$ sites and try to model the CoPc molecular stacks with 3 and 4 active molecules respectively. We assume that $t$ and $U$ take the same values than before and that there is one electron per site in the ground state. We label the sites from $n = 1$ to $n = N$, starting from the molecule closest to the tip. For $N = 3$, the ground state and first excited state have $S = 1/2$ and the second excited state has $S = 3/2$ (see Fig. 3). Thus, we expect two inelastic transitions, at energies $J$ and $3J/2$. For the $N = 4$ chain, the ground state has $S = 0$ and the two lowest energy excited states, both with $S = 1$, have excitation energies 0.7$J$ and 1.4$J$, see Fig. 4. Again, two inelastic steps are expected at those energies.

In Figs. 3(a) and 4(a) we show the conductance for $N = 3$ and $N = 4$ respectively assuming that the electrons can tunnel from the tip to the $n = 1$ site only and from the $n = N$ site to the surface. As in the case of the dimer, we take 3 different values for $E_d$: hole mediated, electron mediated and EHSP. On top of the symmetry trends already discussed for the dimer, we see how in the EHSP only the lowest energy transition is seen both in the $N = 3$ and $N = 4$ cases. This suggests that not only the elastic contribution vanishes, as in the case of the Anderson model and the Hubbard dimer, but also some of the inelastic transitions can be suppressed possibly due to the destructive interference between the hole and electron channels.

In the case of Figs. 3(a) and 4(a), where only the sites at the end of the chain are coupled to either the tip or the surface, the steps are visible for both signs of $V$, at odds with the experimental observations. In an attempt to explore a scenario in which the height of the steps are only visible at a given polarity, we have considered a situation where electrons can tunnel from the tip to sites other than $n = 1$ and from the surface to sites other than $n = N$. By so doing, we can obtain $dI/dV$ curves where the steps are depleted for $V < 0$ (Figs. 3(b) and 4(b)). However, we think that a more plausible explanation would come from a microscopic calculation including more than 1 orbital per molecule. It must also be mentioned the broadening of the excitations observed experimentally is larger than 5.4 $k_B T$, which indicates than neglecting the intrinsic broadening due to the coupling to the continuum of states of the electrodes is not fully justified.

V. MAGNETIC ADATOMS

We now consider spin IETS through a single Mn atom deposited on a Cu$_2$N surface. This system has been widely studied experimentally and theoretically in most instances modeling the Mn spin with an effective spin model. Here we go beyond the spin model picture and we use a multiorbital Anderson Hamiltonian for the 5 $d$ electrons of the Mn$^{2+}$ ion which includes Coulomb interaction, spin-orbit coupling and crystal field. Transport occurs via virtual transitions to the many-body states with either 4 or 6 $d$ electrons. Our approach requires the exact diagonalization of the fermionic model in the 3 relevant charge states, with 4,
5 and 6 electrons. Below we describe the multi-orbital Anderson model, the transport calculation and compare with the experimental results in Ref. [4].

A. Magnetic system Hamiltonian

Here we describe our model Hamiltonian for the Mn ion in the Cu2N surface. The purpose of our model is to provide a minimal fermionic Hamiltonian that accounts for the data, rather than to provide a realistic description of the Mn ion on the surface. Density functional calculations [22, 23, 24] suggest that the Mn adatom transfers charge to the CuN surface and creates bonds with its neighboring N atoms. As a result, the Mn adatom becomes a Mn$^{2+}$ ion that has lost its two $4s$ electrons. We model this system considering only the $3d^5$ electrons of the Mn, including the electrostatic potential of the neighboring atoms. The Hamiltonian of the MS can be written as:

$$\hat{H}_C = H_{ee} + H_{CF} + H_{SO} + H_{Zee},$$  \hspace{1cm} (26)

where $H_{ee}$ is the Coulomb repulsion between the $3d$ electrons, $H_{CF}$ is the crystal field Hamiltonian, $H_{SO}$ is the spin-orbit Hamiltonian and $H_{Zee}$ is the Zeeman Hamiltonian associated to an applied magnetic field $\vec{B}$. The Coulomb matrix elements of the atomic orbitals can be expressed in terms of radial integrals which depend on the specific form of the approximate wave function and an angular part that can be obtained analytically. We have taken them from a calculation for an isolated ion using Gaussian package [25], which yields to the unscreened on-site Coulomb repulsion $U \simeq 24$eV, in accordance with unscreened Hartree-Fock calculations. Since screening in the real system makes $U$ much smaller than the single ion calculation we have downscaled the Coulomb matrix elements with an overall dielectric constant of $\varepsilon = 4.7$ in order to obtain $U$ in the range of 5eV [48].

The energy $E_d$ of the $d$ levels before crystal splitting is included, is kept as a free parameter in our theory. The crystal field term $H_{CF}$ is built using a point charge model for the first N and Cu neighbors whereas an effective dielectric constant $\varepsilon'$ was introduced to account for the screening of the bare crystal field and fit the many-body spectrum to that of the single ion Hamiltonian. Fig. 3(a) shows the splitting of the five $d^5$ energy levels due to the crystal field, together with its dominant orbital contribution. Finally, the spin-orbit Hamiltonian reads:

$$H_{SO} = \sum_{m,m',\sigma,\sigma'} \langle m\sigma | \vec{L} \cdot \vec{S} | m'\sigma' \rangle d^\dagger_{m\sigma} d_{m'\sigma'}$$  \hspace{1cm} (27)

where $\lambda = 43$meV corresponds to the value of the bare Mn$^{2+}$ ion [50] and $\varepsilon''$ is another free parameter in our model.

The Hamiltonian (26) corresponding to the $3d^5$ electrons was then diagonalized in the space of the 252 possible configurations, using the configuration interaction (CI) method. Analogously, the eigenvalues and eigenvectors of the $3d^4$ and $3d^6$ configurations were calculated in order to get the transition rates [51]. The condition of stable configuration with $N_e = 5$ electrons require that $E_G(5) \leq E_G(4), E_G(6)$. In our case, this bound translates into the inequality $-24.1$eV $< E_d < -18.9$eV. In particular, we choose $E_d$ in the middle of this energy window and, as it will be shown in next section, results do not change significantly with $E_d$.

B. Mn$^{2+}$ energy spectra

According to first Hund’s rule, we expect that the spin of the ground state for the half filled $d$ shell is $S = 5/2$, which is what we obtain from the diagonalization of the model. The sixfold degeneracy at zero field is broken by the combined action of spin-orbit and crystal field. Due to the spin-orbit coupling, the total spin $S$ and total angular momentum $L$ are no longer good quantum numbers. However, our CI method allows to calculate any of these expectations values. We have verified that for our calculation for the Mn$^{2+}$, $\langle S \rangle \approx 5/2$, while $\langle L \rangle \approx 0$, with a deviation smaller than 0.1%. In the same way, $S_z$ is almost a good quantum number.

The location of the first neighbors of Mn is taken from reference [4]. The values of $\varepsilon'$ and $\varepsilon''$ are taken so that the lowest energy levels of the energy spectra obtained from the diagonalization of (26) are in agreement with those of the single ion Hamiltonian, as shown in the Fig 5(b). At zero field, the lowest energy doublet corresponds to $\langle S_z \rangle \approx \pm 5/2$. For the two pairs of excited levels, we get $\langle S_z \rangle \approx \pm 3/2$ and $\langle S_z \rangle \approx \pm 1/2$, in order of increasing energy. Fig. 5(b) shows the magnetic field dependence of the low energy spectra of the Mn$^{2+}$ obtained using the CI calculation, together with the fitting to a phenomenological spin model [26, 27].

$$\hat{H}_S = D S_z^2 + E(S_x^2 - S_y^2) + g\mu_B \vec{B} \cdot \vec{S}.$$  \hspace{1cm} (28)

The first two terms in Eq. (28) describe the single ion magneto-crystalline anisotropy while the last one corresponds to the Zeeman splitting term under an applied magnetic field $\vec{B}$. The main magnetization direction $z$ in Eq. (28) depends on the substrate and magnetic atom nature. In the case of the Mn on a Cu$_2$N substrate, the $z$-axis is perpendicular to the surface. This result is also reproduced by our model [26].

C. Transport

Once the many-body eigenstates of Hamiltonian (26) are obtained, we are in position to study transport through the magnetic atom. For that matter, we need to specify the coupling of the $5d$ orbitals to the tip and the substrate. As the $dI/dV$ spectra was recorded with the tip located exactly over the Mn atom, we will assume
that the tip-atom tunneling is dominated by tunneling between the tip apex $s$ orbital and the $d_{3z^2-r^2}$ oriented along the adatom-tip axis. For the coupling with the substrate, the situation is significantly more complicated and we couple equally all the $d$-orbitals to the substrate, i.e., $V_{S,i} = V_S$. For simplicity, we will omit the coupling between the $s$-orbital of the Cu atom and the empty $s$-orbital of the Mn$^{2+}$ ion at odds with existing DFT calculation. Another important parameter to properly account for the transport properties of the system is the Fermi level of the electrodes. Here we have assumed that the Fermi level of the Cu substrate coincides with its bulk Fermi level, $E_F = -7\text{eV}$. 

The resulting $dI/dV$ is plotted in Fig. 6(a), were the elastic, inelastic and total differential conductance are plotted. Our calculation reproduces both the line-shape of the $dI/dV$ curves as well as the the relative contribution between the elastic and inelastic parts, $G_{inel}/G_{el} \approx 0.5$. Within the model this ratio depends on the position of the charging energies of the atom, $\mu_e$ and $\mu_h$, with respect to the chemical potential of the electrodes. In Fig. 6(b) we show ratio $G_{inel}/G_{el}$ as a function of the on-site energy level $E_d$ in the window of energies where the system ground state contains 5 electrons. As observed, the ratio $G_{inel}/G_{el}$ varies smoothly between 0.4 and 0.6. Thus, our model yields a large inelastic signal, consistent with the experiments, without fine tuning the on-site energy $E_d$. Notice that in the case of Mn on Cu$_2$N at $T = 0.4\text{K}$, the thermal broadening of the inelastic step is such that the inelastic conductance is non-zero even at zero bias.

VI. DISCUSSION AND CONCLUSIONS

We have shown that the inelastic tunneling spectroscopy widely used to study magnetic molecules and atoms adsorbed on surfaces, can be understood in terms of cotunneling. As the electrons go from the tip to the surface, the magnetic system must undergo virtual transitions to states with an extra electron or an extra hole. This picture holds both for elastic tunneling, in which case the MS returns to the original state after the virtual charging process, and inelastic tunnel, for which the state before and after the virtual charging are different. Thus, the origin of both elastic and inelastic conductance is the same, which accounts for the large inelastic signal reported experimentally in a variety of systems, including Mn, Fe and Co on Cu$_2$N or Fe on InSb. Further support to this claim comes from comparison of the evolution of the $dI/dV$ as a function of an applied magnetic field of a quantum dot with a single resident electron in the Coulomb Blockade regime and a single Cobalt atom on Cu$_2$N, both undergoing a transition from the Kondo regime at low field to inelastic steps at large field. Both systems show very similar $dI/dV$. In addition, our microscopic theory provides a natural starting point to describe both the appearance of Kondo correlations, and their relation to the inelastic spin flips in the context of magnetic adatoms and molecules.

Our approach is based on the derivation of an effective cotunneling Hamiltonian acting only in the space of neutral configurations of the MS. The calculation of the effective Hamiltonian requires the exact diagonalization of the MS in the neutral subspace as well as the subspaces with one extra electron and one extra hole. From the formal point of view our results are in agree-
ment with previous works based on a truncation of the $T$-matrix to second order in the coupling Hamiltonian. Our approach permits to obtain an effective cotunneling Hamiltonian that can be compared with effective Kondo-like Hamiltonians proposed in most theoretical analysis of IETS experiments.

We have also explored the origin of the experimentally observed asymmetry with respect to bias inversion in the $dI/dV$ curves. It comes from a combination of two ingredients. First, we need to consider that the bias voltage results in a shift of the chemical potential in the tip, the one in the surface remaining constant. Second, the energy level alignment of the MS must be such that one of the cotunneling channels, either virtual electron addition or virtual hole addition, is dominant.

In summary, we propose a method to describe single spin inelastic electron tunneling spectroscopy which does not rely on effective spin models to describe both the magnetic system and the spin-flip assisted tunneling. Our approach provides a natural explanation for the large inelastic signals observed experimentally, and a microscopic mechanism for the spin assisted tunneling.

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Appendix A: Effective tunneling Hamiltonian

We now use Eq. (4) to derive an effective Hamiltonian which acts on the reservoir fermions and on the $q_0$ subspace of the central island only. By so doing, we shall eliminate the $d^i$ and $d$ operators from the effective Hamiltonian and, more important, we shall obtain a tunneling Hamiltonian for which the current can be derived straightforwardly. The matrix element between any two states in the $q_0$ manifold can be written as:

$$\langle N | \hat{V}_{\text{tun}} | N' \rangle = \langle \Psi_f(0) | (n| \hat{V}_{\text{tun}} | \Psi_f(0)) | n' \rangle,$$  \hspace{1cm} (A1)

where $|N \rangle \equiv |n \rangle \otimes |\Psi_f(0)\rangle$, with $|\Psi_f\rangle$ a multi-electronic Slater state describing independent Fermi seas of left and right electrodes. Importantly, the unperturbed states are product states of the left and right electrodes and the central island. These states can describe both, the ground state of the MS with no excitations in the electrodes and excited states with an electron-hole pair in the electrodes and a excited state $n'$ in the central island. Notice that the electron-hole pair can be either in one electrode or split in the left and right electrodes. In the second case, this excitation contributes to the net current flow. Now we need to evaluate matrix elements like

$$\langle \Psi_f(0) | (n| \Psi_f(0) | (n| V^+ | M_-) = \sum_{\alpha,\beta} V^+_{\alpha,\beta} \langle \Psi_f(0) | f_{\alpha} | \Psi_f(0) \rangle | n \rangle | d^i | m_- \rangle.$$  \hspace{1cm} (A2)

Before going further, it is convenient to write down the explicit form of the electrodes wavefunctions. If we denote the ground state of the electrodes in the Fermi sea with no excitations and in its neutral charge state as $|0 \rangle$, we can write $|\Psi_f(0)\rangle = f_{\beta}^\dagger f_{\alpha}^\dagger |0\rangle$, where we are creating an electron-hole pair with quantum number $\alpha$. For the states with one electron excess (defect) we will have $|\Psi_f(+\gamma)\rangle = f_{\beta}^\dagger f_{\alpha}^\dagger |0\rangle$.

The matrix element of the electrode operator in Eq. (A2) selects one and only one term in electrode part of the sums $\sum_{M-} = \sum_{m-} \sum_{m_f}$. The term in question is such that

$$|\Psi_{m_f}(\gamma)\rangle = f_{\gamma}^\dagger |\Psi_f(0)\rangle.$$  \hspace{1cm} (A3)

This relation is equivalent to write $\langle \Psi_f(0) | f_{\gamma} | \Psi_f(0) \rangle = (1 - n_f(\gamma)) \delta_{\beta\gamma}$. We can now write

$$\langle N | \sum_{M-} V^+ | M_- \rangle \langle M_- | V^- | N' \rangle = \sum_{m-} \sum_{m_f} [1-n_f(\alpha)]$$
$$\times \frac{V^+_{\alpha,\beta} V^+_{\alpha',\beta'}}{E_{M-} - E_0 + \epsilon_{\alpha'}} \langle \Psi_f(0) | f_{\beta}^\dagger f_{\alpha'}^\dagger \psi_f(0) \rangle$$
$$\times \langle n | d^i | m_- \rangle \langle m_- | d^i | n' \rangle.$$  \hspace{1cm} (A4)

A similar expression can be obtained for the matrix elements involving states $|M_+\rangle$,

$$\langle N | \sum_{M_+} V^- | M_+ \rangle \langle M_+ | V^+ | N' \rangle = \sum_{m_+} \sum_{m_f} n_f(\alpha)$$
$$\times \frac{V^-_{\alpha,\beta} V^-_{\alpha',\beta'}}{E_{M+} - E_0 - \epsilon_{\alpha'}} \langle \Psi_f(0) | f_{\beta}^\dagger f_{\alpha'}^\dagger \psi_f(0) \rangle$$
$$\times \langle n | d^i | m_+ \rangle \langle m_+ | d^i | n' \rangle.$$  \hspace{1cm} (A5)

Now, it is straightforward to show that the addition of Eqs. (A4)-(A5) leads to the final expression (5).

Appendix B: Tunneling transition rates

As stated in the Sec. II B, the cotunneling transition rates can be calculated applying the Fermi Golden Rule to the effective tunneling Hamiltonian $\hat{H}_{\text{tun}}$. Introducing the density of states $\rho_{\eta\eta'}$ and using Eqs. (A4)+(A5), the transition rate from a state $n'$ of the central island to an state $n''$, with the transport electron going from electrode $\eta$ to $\eta'$ and its spin from $\sigma$ to $\sigma'$, are given by
\[ W_{n,n'}^{n\sigma' n'\sigma} = \frac{2\pi}{\hbar} \int d\epsilon \rho_{n\sigma}(\epsilon) \rho_{n\sigma}(\epsilon + \Delta_{nn'}) f(\epsilon - \mu_n) \left( 1 - f(\epsilon + \Delta_{nn'} - \mu_{n'}) \right) \times \left| \langle n| \hat{O}_{n\sigma, n'\sigma}^{(+)}(\epsilon, \epsilon + \Delta) | n' \rangle - \langle n'| \hat{O}_{n'\sigma, n\sigma}^{(-)}(\epsilon + \Delta, \epsilon) | n \rangle \right|^2 , \tag{B1} \]

with \( \Delta_{nn'} = E_n - E_{n'} \) and \( f(\epsilon) \) the Fermi-Dirac distribution. The matrix elements of the \( \hat{O}(\pm) \) operators in Eq. [31] are defined as

\[ \langle n| \hat{O}_{n\sigma, n'\sigma}^{(+)}(\epsilon, \epsilon + \Delta) | n' \rangle = \sum_{ii', m_{ii'}} V_{n,i}(\epsilon) V_{n',i'}^{*}(\epsilon') \gamma_{nn'}^{m_{ii'}}(ii', \sigma\sigma') \]

and

\[ \langle n'| \hat{O}_{n'\sigma, n\sigma}^{(-)}(\epsilon + \Delta, \epsilon) | n \rangle = \sum_{ii', m_{ii'}} V_{n',i}(\epsilon + \Delta) V_{n,i'}^{*}(\epsilon') \gamma_{nn'}^{m_{ii'}}(ii', \sigma\sigma') , \]

where we have used a simplified notation \( V_{n,i}(\epsilon) \equiv V_{n,i}(\epsilon, \epsilon, \epsilon, \epsilon') \). These transitions rates are in perfect agreement with the rates obtained by a second order truncation of the \( T \)-matrix.\textsuperscript{36,37}

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