Quantum coherence driven magnetic ordering in biased three level coordination compounds

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Novel understanding of the recent nanomagnet tailoring experiments and the possibility to further unveil the mechanisms by which the magnetic interactions arise in an atom by atom fashion covers importance as the demand for spin qubit and quantum state detection architectures increases. Here, we address the spin states of a molecular trimer comprising three localized spin moments embedded in a metallic tunnel junction and show that the pair spin interactions can be engineered through the electronic structure of the molecular trimer. We show that bias and gate voltages induce either a completely ferromagnetic state of the localized moments or a spin frustrated state with different stabilities, and that switching between these states is possible on demand by electrical control. The role of quantum coherence in the molecular trimer is discussed with regards to the spin ordering as well as the interplay among electronic interference and induced dephasing by the metallic leads. This work sets foundations for more robust all electrically controlled spin architectures usable in quantum engineering systems and serves as a test bench for exploring unresolved questions in magnetic ordering and symmetry.

I. INTRODUCTION

Engineering magnetism at the atomic scale has emerged as one of the most vibrant, interesting and challenging areas of study in the field of condensed matter in the last decade. Fueled by novel experimental techniques developed in the context of scanning tunneling microscopy (STM), scientists have been empowered to manipulate, control and probe matter at atomic scale resolution [1, 2]. The manipulation of atomic spins has yet captured much of the focus and effort of experimental nanotechnology [3–5]. Driven by the need to produce novel quantum states of matter optimal for the use in quantum information and quantum engineering applications as well as for emergent spintronic technology [8, 41], it is desired to tune spin-spin interactions to either ferromagnetic or to antiferromagnetic alignment [4, 9] with stable single spin anisotropy.

The magnetic interactions, both in sign and magnitude, which respectively provide ferro- or antiferromagnetic couplings between spins, as well as magnetic anisotropies, can be adjusted through indirect spin interactions by properly orienting and separating the magnetic ions in the molecule being adsorbed [4]. On the other hand, the indirect interactions are completely determined by the electronic structure of the substrate, what suggests that engineering the density of states of the host will influence the sign and magnitude of the effective exchange coupling among the spins grafted onto it through the Kondo interaction [4, 9–11].

By invoking the results in [12, 15? ? , 16], the transport properties of molecular junctions, particularly the (differential) conductance, can be hindered or enhanced depending on the nature and origin of quantum interference present within the molecular structure of interest. A manifestation of this has been shown to be intimately related with the conjugation order of the molecule, whether broken, cross or linear [17, 18, 39], and its bonding position with the electrodes or with the linking group, whether para, meta or ortho [16].

Theoretical predictions have confirmed the observed low conductance in junctions under the influence of destructive quantum interference or even in the presence of quantum decoherence [21? ], which is a condition that as well arises in magnetic tunneling junctions of a dimer of spins resembling the experiment reported in [8], when both units are anti-ferromagnetically coupled. Following the same logic, it should in principle be possible to engineer spin-spin interactions in magnetic tunneling junctions by controlling the degree of quantum interference and the emergence of electronic decoherence allowed by the density of electron states, both in sign and magnitude. Here, the fully anti-ferromagnetic interaction is expected to localize the electron states in each energy level available for occupation whereas the fully ferromagnetic interaction is expected to delocalized the electron wave in the molecule, hence, favoring quantum coherence of different nature [? ].

In this context, according to the work of [4, 22–24] where frustrated spin geometries have been engineered, completely ferromagnetic ordered, have been tailored, investigations on the effect of electronic quantum coherence and the emergence of decoherence is of great relevance and impact for the studies of open questions in atomic magnetism and in designing building blocks for quantum engineering systems. These issues pose giant challenges for experiments and theory.

The above arguments converge in the grounds of tailoring effective spin ordering by the coordinated action of gate and bias potentials, giving rise of what we call the magnetic $V_{SD}$–$V_G$ diagram. Subsequently these interactions can be probed
using all-electrical measurements as predicted in [25], a completely unexplored issue both from the perspective of non-equilibrium nanophysics and from the point of view of nanotechnology and manipulation at the atomic scale.

II. MODEL

Here, in the present work, we consider a trimer of magnetic ions immersed in an organic molecule that can be a phthalocyanine, a metal hydride such as M-porphyrin, where the M denotes a transition metal element, or an organometal [21? ], exhibiting the possibility of quantum interference whether destructive or constructive. The magnetic ions, which display a localized magnetic moment, do not interact directly, but only through the electron interactions in the host molecule, therefore, the spin-spin interactions are tuned via the molecular electronic structure. The magnetic-ion molecule system is adsorbed onto a metallic substrate, and then probed by a metallic STM tip. As such the Hamiltonian of the system – magnetic ion–molecule–substrate is given by:

\[ \mathcal{H} = \mathcal{H}_{\text{tip}} + \mathcal{H}_{\text{ion}} + \mathcal{H}_{\text{molt}} + \mathcal{H}_{\text{substr}} + \mathcal{H}_{\text{hyb}}, \]  

\[ \mathcal{H}_{\text{tip}} = \sum_{\ell \sigma} \epsilon_{\ell \sigma}(t) c_{\ell \sigma}^\dagger(t) c_{\ell \sigma}(t), \]  

\[ \mathcal{H}_{\text{substr}} = \sum_{\ell \sigma} \epsilon_{\ell \sigma}(t) c_{\ell \sigma}^\dagger(t) c_{\ell \sigma}(t), \]  

\[ \mathcal{H}_{\text{molt}} = \sum_{m \sigma} \epsilon_{m \sigma} d_{m \sigma}^\dagger(t) d_{m \sigma}(t) + \sum_{mn \sigma} \gamma_{mn \sigma} d_{m \sigma}^\dagger(t) d_{n \sigma}(t), \]  

\[ \mathcal{H}_{\text{id}} = \sum_{m} J_{m} s_{m}(t) \cdot S_{m}(t), \]  

\[ \mathcal{H}_{\text{tip-mol}} = \sum_{m \sigma} v_{m \sigma \ell} c_{\ell \sigma}^\dagger(t) d_{m \sigma}(t) + \text{H.c.}, \]  

\[ \mathcal{H}_{\text{substr-mol}} = \sum_{m \sigma} v_{m \sigma} c_{\ell \sigma}^\dagger(t) d_{m \sigma}(t) + \text{H.c.}. \]

The system described through the Hamiltonian given in Eq. (1), is illustrated in Fig. 1.

In the model presented by Eq. (1), \( \mathcal{H}_{\text{tip}} \) represents the Hamiltonian of the metallic tip, \( \mathcal{H}_{\text{substr}} \) the Hamiltonian for the metallic substrate, \( \mathcal{H}_{\text{molt}} \) is the molecular Hamiltonian, the local interaction between the magnetic ion and the conduction electrons is given by \( \mathcal{H}_{\text{id}} \) and the Tip-Molecule and Substrate-Molecule hybridization are given by Hamiltonians \( \mathcal{H}_{\text{tip-mol}} \) and \( \mathcal{H}_{\text{substr-mol}} \). The parameters defined in the model Hamiltonian are defined as follows: \( \epsilon_{\ell \sigma}(t) \) and \( \epsilon_{\ell \sigma}(t) \) are the energy bands of the metallic tip and the metallic substrate respectively, \( \epsilon_{m \sigma} \) is the energy of the \( m - \ell \) molecular orbital, \( J_{m} \) is the Kondo coupling between the \( m - \ell \) spin moment of the electron with energy \( \epsilon_{m \sigma} \) and the \( m - \ell \) localized spin moment denoted as \( S_{m}(t) \), and, \( v_{m \sigma \ell} \) and \( v_{m \sigma \ell} \) are the overlap integrals between wave functions from the tip and the molecule, and the substrate and the molecule respectively.

The Green’s function for the model represented by Eq. (1), can be obtained from the inverse of the retarded Green’s function given by expression A2. By inverting equation A3, the retarded Green’s function is evaluated, and the lesser and greater Green’s functions are obtained from

\[ G^{<\sigma}(\omega) = \frac{(\pm i)}{\hbar} \sum_{\chi \rho} f_{\chi \rho}^{(4)}(\pm \epsilon) G_{m \sigma \rho}(\omega) \Gamma^{<\rho}(\omega)^{\dagger} G_{m \sigma \rho}^{<\chi}(\omega), \]  

where \( \epsilon \) and \( \omega \) are related through \( \epsilon = \hbar \omega + \chi \) indexes the lead, whether \( \alpha \) for the left lead, or \( \beta \) for the right lead. In Eq. (2), the matrix \( \Gamma^{<\rho}(\omega) \) is proportional to the imaginary part of the retarded self-energy \( \Sigma^{<\rho}(\omega) \) which can be paramterized by (see appendix A)

\[ \Sigma^{<\rho}(\omega) = \Lambda^{<\rho}(\omega) - \frac{i}{2} \Gamma^{<\rho}(\omega). \]  

Here, \( \Lambda^{<\rho}(\omega) \) is related to the Lamb-Shift [26, 27] and \( \Gamma^{<\rho}(\omega) \) represent the coupling between the leads and the molecular energy levels. The diagonal matrix elements of the latter stands for the level broadening, and the off-diagonal matrix elements are related to the dephasing among levels coupled to the reservoir [28, 30? , 31]. To determine the form of matrix element \( \Gamma_{mn \sigma}^{<\rho} \), we consider the definition from [28] of the retarded self-energy matrix element:

\[ \Sigma^{<\rho}_{mn \sigma}(\omega) = \sum_{k} \frac{v_{m \sigma k}^{<\rho} v_{n \sigma k}^{<\rho}}{\epsilon - \epsilon_{k \sigma} + i \delta}. \]  

In the above expression, the couplings \( v_{m \sigma k}^{<\rho} \) and \( v_{n \sigma k}^{<\rho} \) appearing in the model Hamiltonians given by Eqs. (11) and (1g), are complex in nature, and therefore, we can express both of them as an amplitude times a phase factor of the form \( v_{m \sigma k}^{<\rho} = |v_{m \sigma k}| e^{-i \phi_{m \sigma k}} \) and \( v_{n \sigma k}^{<\rho} = |v_{n \sigma k}| e^{i \phi_{n \sigma k}} \), to transform Eq. (4) into

\[ \Sigma^{<\rho}_{mn \sigma}(\omega) = \sum_{k} \frac{|v_{m \sigma k}| |v_{n \sigma k}| e^{-i (\phi_{m \sigma k} - \phi_{n \sigma k})}}{\epsilon - \epsilon_{k \sigma} + i \delta}. \]  

From Eq. (5), we thus, define the elements \( \Gamma_{mn \sigma}^{<\rho} \) according to

\[ \Gamma_{mn \sigma}^{<\rho} = 2\pi \sum_{k} \frac{\delta(\epsilon - \epsilon_{k \sigma}) |v_{m \sigma k}| |v_{n \sigma k}| e^{-i (\phi_{m \sigma k} - \phi_{n \sigma k})}}{\epsilon - \epsilon_{k \sigma} + i \delta}, \]  

where phases \( \phi_{m \sigma k} \) and \( \phi_{n \sigma k} \) determine the strength of the dephasing between levels \( m \) and \( n \). Moreover, it becomes crucial to determine the density of electron states \( \rho_{n}(\omega) \) in the quest for an understanding on what is the interplay between electronic structure and magnetism in the sample. The former can be obtained from the equation

\[ \rho_{n}(\omega) = \frac{i}{2\pi} \sum_{mn \sigma} \sigma_{mn \sigma}^{(0)} (G^{<\sigma}_{mn \sigma}(\omega) - G^{<\sigma}_{mn \sigma}(\omega)), \]  

and similarly, the spin density of states

\[ \rho_{n}(\omega) = \frac{i}{2\pi} \sum_{mn \sigma} \sigma_{mn \sigma}^{(0)} (G^{<\sigma}_{mn \sigma}(\omega) - G^{<\sigma}_{mn \sigma}(\omega)). \]  

In addition to the latter, it is often useful to think about magnetic ordering and change in magnetic configuration in terms
The ordered Green’s function density matrix has been defined with the aid of the contour von Neumann expression obtained from Eq. (9), where the interaction between the electronic level and the localized spin is not shown in arrow form due to lack of space and to keep clarity on where the interactions are and how they are labeled. The above formulation for the spin entropy derives from the von Neumann expression [32] given by

\[ S_{\sigma} = -\rho_{\sigma} \ln \rho_{\sigma}, \]  

where \( \rho_{\sigma} \) denotes the density matrix of the system, we can write, a general expression in terms of contour Green’s functions for the entropy associated with spin degrees of freedom can be written

\[ S_{\sigma} = -i\hbar \int \frac{d\omega}{2\pi} \left[ G^{<}_{\sigma\sigma}(\omega) \ln(-i\hbar G^{<}_{\sigma\sigma}(\omega)) \right] \frac{d\omega}{2\pi}. \]  

The above formulation for the spin entropy derives from the von Neumann expression obtained from Eq. (9), where the density matrix has been defined with the aid of the contour Green’s function \( G^{<}_{\sigma\sigma}(\omega) \) in matrix form

\[ \rho_{\sigma} = \begin{pmatrix} d_{\sigma r} & d_{\sigma r}^\dagger \\ d_{\sigma r} & d_{\sigma r}^\dagger \end{pmatrix} \begin{pmatrix} d_{\sigma r} & d_{\sigma r}^\dagger \\ d_{\sigma r} & d_{\sigma r}^\dagger \end{pmatrix} = -i\hbar G^{<}_{\sigma\sigma}(\omega). \]  

Here we approach the question of the emergence of quantum interference and its relationship to the spin configuration of the molecule of interest. A useful theoretical tool available from the Landauer formalism [28] to determine the degree of quantum interference in a molecular conductor is the Transmission probability given by

\[ T_{\alpha\beta}(\epsilon) = \text{tr} G^{R}(\omega)\Gamma^{(\alpha)} G^{A}(\omega)\Gamma^{(\beta)}. \]  

From the same viewpoint, other theoretical tools such as particle and energy currents have lead to useful predictions in systems relevant for the discussion of the present paper [9, 21?], and therefore we have considered them into the investigation here reported. These transport quantities are written according to

\[ J_{N}^{(x)} = -\frac{1}{\hbar} \sum_{\sigma} \int \left( f_{\chi\sigma}(\epsilon) - f_{\chi\sigma}(\epsilon) \right) T_{\chi\chi}(\epsilon) d\epsilon, \]  

\[ J_{E}^{(x)} = -\frac{1}{\hbar} \sum_{\sigma} \int \epsilon( f_{\chi\sigma}(\epsilon) - f_{\chi\sigma}(\epsilon) ) T_{\chi\chi}(\epsilon) d\epsilon, \]  

where \( \chi \) refers to the lead on the opposite side to \( \chi \) of the junction.

Along the same line, we study the quantum interference present in the molecule with regards of the trimmer spin structure with an analytic expression for the differential charge conductance:

\[ \sigma_{\chi} = \frac{\partial J_{N,\chi}^{x}}{\partial V} \]  

We recall some important quantities when computing the current observables for the quantum transport in stationary regime, regarding the flow of particles from both leads to the molecule and vice-versa. First, from the number operator \( \hat{N} \) written from a field operator simplified form we define the particle current as:

\[ J_{N}^{x} = \langle \frac{d\hat{N}}{dt} \rangle \]  

where we can see that \( J_{N}^{x} = -e J_{N}^{x} \) can be defined as the charge current or the current of electrons. Now, from the first law of thermodynamics:

\[ J_{N}^{x} = J_{E}^{x} + \mu_{\chi} J_{N}^{x} \]  

In (16), \( J_{E}^{x} \) is the heat current from lead \( \chi \) to the molecule, and \( J_{N}^{x} \) is the energy current. \( \mu_{\chi} \) stands for the chemical potential in lead \( \chi \) defined from a symmetrical protocol that we will specify in a moment. We obtained some expressions for these currents in Keldish contour using non-equilibrium Green’s Functions [28]. For the heat current we have:

\[ J_{E}^{x} = -\frac{1}{\hbar} \int \frac{d\epsilon}{2\pi} (-\mu_{\chi}) T_{\chi} \left[ \text{Tr} \Gamma^{(\chi)} \left( G^{<}(\epsilon) f_{\chi}(\epsilon) + G^{<}(\epsilon) f_{\chi}(-\epsilon) \right) \right] \]  

In (17), \( \Gamma_{\chi\chi}(\epsilon) = \) is the Gamma matrix of (6) for the couplings with the leads (which is \( \mu_{\chi} \) independent and \( A(\epsilon) \) is the
density of states in the molecule. \( f_x(e) \) is the Fermi function for the leads. We note that \( f_x(-e) = 1 - f_x(e) \).

We start from the following equations:

\[
J_x^e = -ie \int de \text{Tr} \left[ \Gamma^\nu(e) \left[ G^\nu(e) f_x(e) + G^\nu(e) f_x(-e) \right] \right] \tag{18}
\]

\[
G^{\gamma<\gamma}(e) = G^R(e) \Sigma^{\gamma<\gamma}(e) G^A(e) \tag{19}
\]

\[
\Sigma^{\gamma<\gamma}(e) = \mp i \sum_x f_x(\mp e) \Gamma^\nu(e) \tag{20}
\]

For the equations above: (19) is the Keldish equation for \( G^R \) and \( G^\nu \) in energy domain, and (20) is the self energy of the molecule following the formalism in [28]. We obtain an expression for (14) in stationary regime by assuming that both \( G^{R,A} \) do not depend on the chemical potential since the problem is not a self-consistent one. With this in mind let’s start. An expression for \( f_x'(e) \) (we let \( x = \beta(\epsilon - \mu_x) \))

\[
f_x'(e) = \frac{\partial}{\partial \mu_x} \left( \frac{1}{1 + e^{\beta(\epsilon - \mu_x)}} \right) = \frac{\beta e^{\beta(\epsilon - \mu_x)}}{(1 + e^{\beta(\epsilon - \mu_x)})^2} \]

Using \( 2 \cosh(x) = e^x + e^{-x} \) we obtain:

\[
f_x'(e) = \frac{\beta}{2 \cosh(x/2)^2} = \frac{\beta}{4} \cosh^{-2}(x/2) \]

Finally, we obtain:

\[
f_x'(e) = \frac{\partial f_x}{\partial \mu_x} = \frac{\beta}{4} \cosh^{-2} \left( \frac{\beta(\epsilon - \mu_x)}{2} \right) \tag{21}
\]

Now we use (20) and we write:

\[
\Sigma^\nu(\epsilon) = -i \sum_x f_x(\mp e) \Gamma^\nu(e)
\]

\[
\Sigma^\nu(\epsilon) = i \sum_x f_x(e) \Gamma^\nu(e) = i \left[ \Gamma L f_L(e) + \Gamma R f_R(e) \right]
\]

From this expression, we can write: (Let \( \Gamma(\epsilon) = \Gamma L(e) + \Gamma R(e) \))

\[
\Sigma^\nu = -i \left[ (1 - f_L(e)) \Gamma L + (1 - f_R(e)) \Gamma R \right]
\]

\[
= -i \left[ \Gamma L + \Gamma R \right] + \Sigma^\nu(\epsilon)
\]

\[
\Sigma^\nu(\epsilon) = \Sigma^\nu(\epsilon) - i \Gamma(\epsilon) \tag{22}
\]

We consider a symmetric protocol configuration for the variations of the chemical potentials in such a way that \( \mu_x = \mu_0 \pm e V/2 \), where \( \mu_0 \) is some reference constant chemical potential and “V” is the bias voltage applied to both leads. Then \( \frac{\partial \mu_x}{\partial V} = \pm \frac{e}{2} \) and we can write:

\[
\sigma^x = \frac{\partial J_x^e}{\partial \mu_x} \frac{\partial \mu_x}{\partial V} = \pm \frac{e}{2} \frac{\partial J_x^e}{\partial \mu_x}
\]

From the previous expression, we see that we need to take the derivatives:

\[
\frac{\partial}{\partial \mu_x} \left( G^R(e) f_x(e) \right) = \frac{\partial G^R}{\partial \mu_x} f_x(e) + G^R f_x'(e)
\]

\[
\frac{\partial}{\partial \mu_x} \left( G^\nu(1 - f_x(e)) \right) = \frac{\partial G^\nu}{\partial \mu_x} \left( 1 - f_x(e) \right) = \frac{\partial G^\nu}{\partial \mu_x} - \frac{\partial G^\nu}{\partial \mu_x} f_x - G^\nu f_x'(e)
\]

From equation (19) together with (20) we have:

\[
\frac{\partial G^{\gamma<\gamma}}{\partial \mu_x} = \frac{\partial}{\partial \mu_x} \left( G^R \Sigma^{\gamma<\gamma} G^A \right) = G^R \frac{\partial}{\partial \mu_x} \left( \Sigma^{\gamma<\gamma} G^A \right),
\]

\[
\frac{\partial}{\partial \mu_x} \left( \Sigma^\nu(\epsilon) \right) = \frac{\partial}{\partial \mu_x} \left[ \Sigma^\nu(\epsilon) - i \Gamma(\epsilon) \right] = \frac{\partial}{\partial \mu_x} \left( \Sigma^\nu(\epsilon) \right) = i \Gamma f_x'^. \tag{24}
\]

Then:

\[
\frac{\partial G^{\gamma<\gamma}}{\partial \mu_x} = i G^R \Gamma f_x' G^A \tag{25}
\]

Using (25) in the derivatives in (24) we find:

### III. SPIN-SPIN EFFECTIVE INTERACTIONS AND ELECTRONIC QUANTUM INTERFERENCE

Effective spin-spin interactions are calculated from the expression derived in ref. [25]. Specifically, in this paper we address the effective Heisenberg exchange interactions present in the system described by the model given in Eq. (1) and illustrated in Fig. 1. These interactions among three localized magnetic moments labeled as \( S_a, S_b, S_c \), that are coupled via Kondo interactions \( J_a, J_b, J_c \), and electrons present in three energy levels \( \epsilon_a, \epsilon_b, \epsilon_c \), respectively, are given by Eq. (82). Here, we pay special attention to two cases of great interest, which are the ferromagnetic state where all effective interactions \( J_{mn} \) are negative, and the antiferromagnetic state where these interactions are now all positive. The stability and control of these ordering, as well as its manipulation and detection can be done by several means, one of them being the all-electrical control as demonstrated for Manganese based metal hydrides [33], among other experimental realizations [8, 34–37]. All-electrical control has also been shown to allow for atom by atom tailoring of nanomagnets [4] through the RKKY interaction including spin-frustrated networks. Moreover, all electrical control has provided a means of control for the singlet-triplet switching in a dimer of Cobalt atoms, and these states were detected by measurements of charge current flowing through the host molecule. In single magnetic unit molecules, important properties have been also engineered with the aid of a bias voltage. Another degree of control possible is the control through gate fields, demonstrated in the Antheraquinone transistor, in which case the destructive quantum
interference exhibited by this type of molecule was lifted by the action of this gate [12]. The latter suggests that a combined bias voltage - gate field control scheme can provide the possibility to switch between spin states determined by the magnetic ordering present in the molecule, and quantum interference, its nature and strength has a strong chance to also play a role in this switching dynamics. The system we address here, combines these means of control, that is, the electric control provided by a bias voltage and control driven by the gate field, as well as the variation of the degree of quantum coherence present in the electronic part of the molecule. The latter is achieved by means of modulating the model given by Eq. (1) with associated Green’s function given by Eq. (A3), in terms of the parameter $\gamma_{ab}$, which varies from 0 to 6 meV, where $\gamma_{ab} = 0$ meV resembles a molecular structure with no possibility to exhibit quantum interference, and as $\gamma_{ab}$ increases, the degree of electronic coherence in the system increases. This way of controlling quantum interference in the multiple sites model, in the electronic $\Lambda-\Delta$ system, was studied in ref. [39]. Here, we extend the investigation by considering a molecule with magnetic units, the question of atom by atom engineered exchange interaction and the interplay among the degree of electronic quantum interference and other means of control, namely a bias voltage and a gate field, in the switching dynamics of magnetic ordering in the molecule of interest, see Fig. 1.

IV. SPIN EXPECTATION VALUES IN THE PRESENCE OF A ZEEMAN MAGNETIC FIELD

With the aim of visualising phase transitions in magnetic ordering of the trimmer, we study the effect of a symmetry breaking phenomenon induced by a Zeeman term in the effective spin-spin Heisenberg interaction Hamiltonian (B1) by means of the spin expectation values given by (B14). The new spin Hamiltonian is:

$$\mathcal{H}_{\text{spin}} = \sum_{m,n} \mathcal{J}_{mn} \cdot S_m \cdot S_n - \Delta \sum_k S_k \cdot B_k$$  \hspace{1cm} (26)

, where $\Delta$ is a constant equal to one in atomic units, and $B_k$ are staggered fields for each localized spin.

The isotropic nature of the Heisenberg effective interaction permits to project each localized spin along the z-direction in particular, without loose of generality, in order to characterize the phase transitions.

V. RESULTS

The voltage, electric field and delocalization induced switching dynamics of the spin ordering in the molecule of interest in the present paper, is demonstrated here, by predicting the variation of the effective exchange interactions among the magnetic units present in the molecules, namely $\mathcal{J}_{ab}$, $\mathcal{J}_{ac}$ and $\mathcal{J}_{bc}$. This variation is shown to be induced by the modulation of three different conditions driving the molecular degrees of freedom. First, parameter $\gamma_{ab}$ is varied in the range $0 \leq \gamma_{ab} \leq 6$ meV. The variation of this parameter, induces a change in spin ordering in the molecule from nearly eight-fold-degeneracy to spin-frustrated state to all ferromagnetic ordering as depicted in the scheme shown in Fig. 2, and as predicted through the evaluation of $\mathcal{J}_{ab}$, $\mathcal{J}_{ac}$ and $\mathcal{J}_{bc}$ shown in Fig. 3, and done by employing Eq. (B2). Moreover, the contour shown in Fig. 4 illustrates how the modulation of $\gamma_{ab}$ has an effect on the spin ordering around zero-bias, for 3 different values for the gate field expressed as an energy $V_G = -7.2$ mV, $-5.6$ mV, $-4.0$ mV. This figure, shows that around zero bias there is a commutation among quantum states with all anti-ferromagnetic spin-spin interactions to those with all fer-

![FIG. 2: Delocalization induced switching dynamics of the spin ordering in the molecular trimer shown in Fig. 1. Once the spin-frustrated state is formed in the molecule, the ferromagnetic alignment in the system can be obtained by tuning intermolecular coupling $\gamma_{ab}$, the source-drain voltage $V_{SD}$, or the gate voltage $V_G$.](image_url)

![FIG. 3: Effective exchange interactions $\mathcal{J}_{ab}$, $\mathcal{J}_{ac}$ and $\mathcal{J}_{bc}$. Among spins $S_a$, $S_b$ and $S_c$. The upper left panel presents the effective exchange interactions $\mathcal{J}_{mn}$ for $m,n = a,b,c$ for the case in which $\gamma_{ab} = 0.0$ mV, exhibiting a weak spin ordering around zero-bias, with $V_G = -4.0$ mV. The strength of this ordering increases as $\gamma_{ab}$ varies from 2.2, 3.4, and 6.0 meV, switching from a frustrated configuration to a ferromagnetic state.](image_url)
romagnetic interactions among spins. For $V_G = -4.0$ mV, the frustrated spin state in the molecules occurs at lower values for the parameter $\gamma_{ab}$, as compared with other values for the gate field. At larger values of $\gamma_{ab}$ for the same gate field $V_G$, the spins align ferromagnetically.

The phenomenological insights and microscopic mechanisms behind the modulation of the parameter $\gamma_{ab}$, can be understood by considering the phenomenon of quantum interference in molecular junctions as discussed in [39], which investigates quantum coherent phenomena in molecular junction with a similar electronic configuration to the one investigated in this paper, with the differentiating factor of having the couplings $T^{\chi \chi}_{ab}$ for $\chi = \alpha, \beta$ exactly equal to zero.

Under this assumption, the variation of $\gamma_{ab}$ from vanishing behavior to an intermediate value resembles the transition of the molecular structure corresponding to Anthracene (linear conjugation) like molecular structure, to Anthraquinone (Cross-Conjugation) like molecular structure where delocalization dominates the electronic processes within the molecule [39]. From the electronic transmission probability calculated for the system of interest from Eq. (12), it can be shown that $\gamma_{ab}$ is associated with the ability for the system to exhibit electronic quantum interference as shown in Fig. 5, [18].

By considering the effect of the spin structure in the ability for the system to exhibit quantum interference, mainly of destructive nature, in Fig. 6 shows that the ordering of the magnetic units in the trimer has a decisive effect of the strength of the transmission dip, the broadening and the localization in energy, showing that the respective increase in magnetic symmetry is complained with the corresponding exhibition of weak quantum interference of destructive nature, and the corresponding decrease in symmetry, is associated with the lifting of coherence in the molecule.

This particular feature of this system, can be understood from considering the spin polarized density of states (see Fig. 7) around zero bias and through a bias window in which the system exhibits clear order. In this particular regime, the spin density of states presents abrupt changes when the order is lost, this around the set value for $V_G$.

An additional mean for controlling the ordering in the magnetic trimer is the bias voltage $V_{SD}$, which induces a non-

FIG. 5: Transmission probabilities for the model considered in [39] for $\gamma_{ac} = \gamma_{bc} = 0$ and $\gamma_{ab} = 3.0$ meV (in blue), $\gamma_{ac} = \gamma_{bc} = 3.0$ meV and $\gamma_{ab} = 0$ meV (in red) and, $\gamma_{ac} = \gamma_{bc} = 3.0$ meV and $\gamma_{ab} = 3.0$ meV (in black with yellow stripes). The latter shows a transmission dip around the Fermi level, which is a clear signature of the presence of destructive quantum interference [17, 39].

FIG. 6: Transmission probabilities for the cases with associated spin ordering shown in Fig. 3. In red the case where no spin structure is modulating the density of states of the molecule, and in blue, the case in which the spin structure induces variations on the density of states. The dotted black line corresponds to the set value for the gate field, which in this cases is $V_G = -4.0$ mV.
FIG. 7: Spin polarization $\rho_s(\omega)$ of the molecule under study for a gate field $V_G = -4.0$ mV.

FIG. 8: Magnetic $V_{SD}-V_G$ diagram. Shows regions where antiferromagnetic ordering arises (coincidence in yellow) and other ones where ferromagnetic ordering does it so (coincidence in blue). The panels are arranged in vertical order for different values of the parameter $\gamma_{ab}$.

FIG. 9: Switching dynamics among ordered spin states as function of the applied gate voltage $V_G$ at zero voltage bias.

By looking now at Fig. 9, one sees the gating conditions for which the anti-ferromagnetic state will be more stable and robust against variations in the gate field and against modulations of the parameter determining the degree of quantum interference $\gamma_{ab}$, for which we determined this condition to be $V_G \approx -4.0$ mV. By changing the gating condition is possible to obtain the all-ferromagnetic configuration for small values of $\gamma_{ab}$, or this can be achieved by stabilizing the gate field around the set value, and rather modulating $\gamma_{ab}$ as shown in the lower right panel of Fig. 9, condition perfectly exemplified in the diagram shown in Fig. 2.

By staring at the contour plots in Fig. 8 it can be seen that there are regions in the $V_{SD}-V_G$ diagram for the effective exchange that correspond to one type of ordering and and by the selecting biasing of the junction, a different state can be engineered, following the line of thought of the experiments reported in [3–5, 10, 41–43], where magnetic excitations in ad-atoms are engineer by the action of electric drives, in many cases, in agreement with the RKKY limit. Here we have explored an additional degree of freedom for controlling this tailoring at the atomic scale, that is, the gate field $V_G$ which provides reasonable tuning possibility among anti-ferromagnetic (AFM) and ferromagnetic (FM) ones as shown in Fig. 9, hence empowering the optimal location of the operating point of the molecule in the magnetic $V_{SD}-V_G$ diagram.

This means of control, as stated before, has been successfully demonstrated in [12]. Now, we will focus on what are the possibilities for tuning either anti-ferromagnetically or ferromagnetically the magnetic units in the probed molecule. Fig. 9, considers the effective exchanges among spins as a function of gate voltage for a zero-bias condition, therefore this prediction cannot be verified by electrical means, though it provides some insight on how to tune the system with the gate field to commute among magnetic configurations, as exemplified in Fig. 2.
VI. EIGEN-VALUE AND EIGEN-STATE ANALYSIS

In the present paper, we are interested in two regimes of ordering: Ferromagnetic and Anti-Ferromagnetic. To determine whether the spin states exhibit classical correlations or quantum entanglement, we analyze the eigen-values and the corresponding eigen-state and the associated Von-Neumann entropy of the effective spin Hamiltonian B.1. Let’s consider two relevant cases, where $J_{ab} = J_{ac} = J_{bc} = \mathcal{J}$ and where $J_{ab} = \mathcal{J}, J_{ac} = J_{bc} = 0$, and determine the spectral diagram for the quantum spin states in both, the ferromagnetic and the anti-ferromagnetic spin ordering.

A. Ferromagnetic Ordering

1. Case: Equal Spin-Spin Effective Couplings

From expression B.13, the eigen-energies of the Spin Hamiltonian give:

$$
\mathcal{E}_{\text{spin}}^{(1)} = \mathcal{E}_{\text{spin}}^{(2)} = \mathcal{E}_{\text{spin}}^{(3)} = \mathcal{E}_{\text{spin}}^{(4)} = -\mathcal{J}; \quad (27)
$$

$$
\mathcal{E}_{\text{spin}}^{(5)} = \mathcal{E}_{\text{spin}}^{(6)} = 3\mathcal{J}; \quad (28)
$$

$$
\mathcal{E}_{\text{spin}}^{(7)} = \mathcal{E}_{\text{spin}}^{(8)} = 3\mathcal{J}; \quad (29)
$$

where the ground state of the Hamiltonian under this conditions is a quartet state $\chi_\mathcal{q}$ given by:

$$
\chi_\mathcal{q} = \begin{bmatrix}
|\uparrow\uparrow\uparrow\\
\frac{1}{\sqrt{3}} (|\uparrow\uparrow\downarrow| + |\uparrow\downarrow\downarrow| + |\downarrow\uparrow\downarrow|)\\
\frac{1}{\sqrt{3}} (|\downarrow\uparrow\downarrow| + |\uparrow\downarrow\uparrow| + |\downarrow\downarrow\uparrow|)\\
|\downarrow\downarrow\downarrow|
\end{bmatrix} \quad (30)
$$

B. Case: Symmetric Coupling

For this case, which is when $J_{ab} = \mathcal{J}, J_{ac} = J_{bc} = 0$, the eigen energies give:

$$
\mathcal{E}_{\text{spin}}^{(1)} = \mathcal{E}_{\text{spin}}^{(2)} = \mathcal{E}_{\text{spin}}^{(3)} = \mathcal{E}_{\text{spin}}^{(4)} = -(\mathcal{J} + 2\mathcal{J}_0); \quad (31)
$$

$$
\mathcal{E}_{\text{spin}}^{(5)} = \mathcal{E}_{\text{spin}}^{(6)} = -\mathcal{J} + 4\mathcal{J}_0; \quad (32)
$$

$$
\mathcal{E}_{\text{spin}}^{(7)} = \mathcal{E}_{\text{spin}}^{(8)} = 3\mathcal{J}; \quad (33)
$$

where the ground state for this case is as well given by 30.

C. Anti-Ferromagnetic Ordering

1. Case: Equal Spin-Spin Effective Couplings

$$
\mathcal{E}_{\text{spin}}^{(1)} = \mathcal{E}_{\text{spin}}^{(2)} = \mathcal{E}_{\text{spin}}^{(3)} = \mathcal{E}_{\text{spin}}^{(4)} = 3\mathcal{J}; \quad (34)
$$

$$
\mathcal{E}_{\text{spin}}^{(5)} = \mathcal{E}_{\text{spin}}^{(6)} = -3\mathcal{J}; \quad (35)
$$

$$
\mathcal{E}_{\text{spin}}^{(7)} = \mathcal{E}_{\text{spin}}^{(8)} = -3\mathcal{J}; \quad (36)
$$

with an associated degenerate doublet as a ground state given by:

$$
\chi_{\mathcal{q}_1} = \begin{bmatrix}
\frac{1}{\sqrt{1 + \gamma_{111}^2 + \gamma_{111}^2}} (\gamma_{111} |\uparrow\uparrow\downarrow| + \gamma_{111} |\downarrow\uparrow\uparrow| + |\downarrow\downarrow\uparrow|)\\
\frac{1}{\sqrt{1 + \gamma_{111}^2 + \gamma_{111}^2}} (\gamma_{111} |\downarrow\uparrow\downarrow| + \gamma_{111} |\uparrow\downarrow\uparrow| + |\downarrow\downarrow\uparrow|)\\
\frac{1}{\sqrt{1 + \gamma_{111}^2 + \gamma_{111}^2}} (\gamma_{111} |\downarrow\downarrow\uparrow| + \gamma_{111} |\uparrow\downarrow\uparrow| + |\downarrow\downarrow\uparrow|)
\end{bmatrix} \quad (37)
$$

$$
\chi_{\mathcal{q}_2} = \begin{bmatrix}
\frac{1}{\sqrt{1 + \gamma_{111}^2 + \gamma_{111}^2}} (\gamma_{111} |\uparrow\uparrow\downarrow| + \gamma_{111} |\downarrow\uparrow\uparrow| + |\downarrow\downarrow\uparrow|)\\
\frac{1}{\sqrt{1 + \gamma_{111}^2 + \gamma_{111}^2}} (\gamma_{111} |\downarrow\uparrow\downarrow| + \gamma_{111} |\uparrow\downarrow\uparrow| + |\downarrow\downarrow\uparrow|)\\
\frac{1}{\sqrt{1 + \gamma_{111}^2 + \gamma_{111}^2}} (\gamma_{111} |\downarrow\downarrow\uparrow| + \gamma_{111} |\uparrow\downarrow\uparrow| + |\downarrow\downarrow\uparrow|)
\end{bmatrix} \quad (38)
$$

D. Case: Symmetric Coupling

$$
\mathcal{E}_{\text{spin}}^{(1)} = \mathcal{E}_{\text{spin}}^{(2)} = \mathcal{E}_{\text{spin}}^{(3)} = \mathcal{E}_{\text{spin}}^{(4)} = \mathcal{J} + 2\mathcal{J}_0; \quad (39)
$$

$$
\mathcal{E}_{\text{spin}}^{(5)} = \mathcal{E}_{\text{spin}}^{(6)} = -3\mathcal{J}; \quad (40)
$$

$$
\mathcal{E}_{\text{spin}}^{(7)} = \mathcal{E}_{\text{spin}}^{(8)} = \mathcal{J} - 4\mathcal{J}_0; \quad (41)
$$

The ground state will depend on whether $\mathcal{J} > \mathcal{J}_0$ or $\mathcal{J} < \mathcal{J}_0$. For $\mathcal{J} > \mathcal{J}_0$, the ground state energy is $E_{G,S} = -3\mathcal{J}$ and the associated eigen-state is given by:

$$
\chi_\mathcal{g} = \begin{bmatrix}
\frac{1}{\sqrt{1 + \gamma_{111}^2 + \gamma_{111}^2}} (\gamma_{111} |\uparrow\uparrow\downarrow| + \gamma_{111} |\downarrow\uparrow\uparrow| + |\downarrow\downarrow\uparrow|)\\
\frac{1}{\sqrt{1 + \gamma_{111}^2 + \gamma_{111}^2}} (\gamma_{111} |\downarrow\uparrow\downarrow| + \gamma_{111} |\uparrow\downarrow\uparrow| + |\downarrow\downarrow\uparrow|)\\
\frac{1}{\sqrt{1 + \gamma_{111}^2 + \gamma_{111}^2}} (\gamma_{111} |\downarrow\downarrow\uparrow| + \gamma_{111} |\uparrow\downarrow\uparrow| + |\downarrow\downarrow\uparrow|)
\end{bmatrix} \quad (42)
$$

For $\mathcal{J} < \mathcal{J}_0$, the ground state energy is $E_{G,S} = \mathcal{J} - 4\mathcal{J}_0$ and the associated eigen-state is given by

$$
\chi_\mathcal{g} = \begin{bmatrix}
\frac{1}{\sqrt{1 + \gamma_{111}^2 + \gamma_{111}^2}} (\gamma_{111} |\uparrow\uparrow\downarrow| + \gamma_{111} |\downarrow\uparrow\uparrow| + |\downarrow\downarrow\uparrow|)\\
\frac{1}{\sqrt{1 + \gamma_{111}^2 + \gamma_{111}^2}} (\gamma_{111} |\downarrow\uparrow\downarrow| + \gamma_{111} |\uparrow\downarrow\uparrow| + |\downarrow\downarrow\uparrow|)\\
\frac{1}{\sqrt{1 + \gamma_{111}^2 + \gamma_{111}^2}} (\gamma_{111} |\downarrow\downarrow\uparrow| + \gamma_{111} |\uparrow\downarrow\uparrow| + |\downarrow\downarrow\uparrow|)
\end{bmatrix} \quad (43)
$$

VII. CONCLUSIONS

In the present reported work we considered a magnetic trimer, with a three level electronic system coupled with its
hosted magnetic units via Kondo interaction, driven by a metallic tunneling junction, such that resembles a scanning tunneling microscopy experiment on magnetic ad-atoms on metallic surface. Additionally, the set up allows for an electric field acting as a gate drive, which in convergence with the bias voltage $V_{DS}$ define a magnetic $V_{DS} - V_G$ diagram where the symmetry status of the magnetic trimer becomes evident. We show that through the following three different mechanisms:

1. Modulation of the nature and strength of the electronic quantum interference,

2. Voltage bias induced non-equilibrium stationary dynamics,

3. Gate field control of the electronic structure [12]

a switching dynamics between all anti-ferromagnetic coupling spin state and all ferromagnetic one can be induced. Interestingly, the results reported for the indirect exchange interaction shown in Figs. 5, 8, 9, showed that not only the orientation but the relative strength or the order can be tuned in the magnetic $V_{DS} - V_G$ diagram for a variety of modulations of the parameter $\gamma_{ab}$, showing the corresponding of the magnetic formation with respect to the control means proposed in this work. Lastly, focusing on the objective of the study, which is to trace a correlation between ordering in the magnetic molecule and coherence in the electronic background, we infer from Fig. 6 that around the set Fermi level by the Gate field $V_G$ (dotted line in black), there is a controlled but prominent (Fano-like dip?) decay in the electronic transmission signing the emergence of the quantum interference of destructive nature. This conclusion, suggests that in the ferromagnetic induced delocalization, the ability to exhibit quantum interference dominates over the quantum coherent phenomena induced by the anti-ferromagnetic localization, in which case entropy driven processes will tend to be robust against anti-ferromagnetic induced electronic decoherence. This conclusion is in agreement with the predictions published in [21] with regards to the competition singlet-triplet formation and orbital localization.

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Appendix A: Evaluation of the Retarded Green’s Function for the Molecular Trimer

The Green’s function, in its retarded form, can be derived from the equation of motion [28] technique as defined for the Keldysh contour, yielding:

$$G_{mnr}(t, t') = \delta_{mn} \delta_{rr'} G_{mrr}(t, t') + \sum_{m_i} \chi_{mn} \int G_{m_{i}rr}(t, \tau) G_{m_{i}m_{i}rr}(\tau, t') d\tau + \sum_{r_i} \int J_{m_i} G_{m_{i}rr}(t, \tau) G_{m_{i}m_{i}rr}(\tau, t') d\tau \tag{A1}$$

where $G_{mrr}(t, t')$ satisfying the Schrödinger-like equation given by:

$$\left( i\hbar \frac{\partial}{\partial \tau} - \varepsilon_{mr} \right) G_{mrr}(t, t') = \delta(t - t').$$

From the model described in Eqs. (1), (A1) defines $[G_{mnr}(\omega)]^{-1}$ such that $G_{mnr}^{R}(\omega) [G_{mnr}^{R}(\omega)]^{-1} = \delta_{mn} \delta_{rr'}$. Thereafter, $[G_{mnr}^{R}(\omega)]^{-1}$ can be written in matrix form in the following way:

$$[G_{mnr}^{R}(\omega)]^{-1} = \begin{bmatrix} \hbar \omega - \varepsilon_{ar} + \frac{i}{2} \Gamma_{ar} & -\gamma_{ab} & -\left( \gamma_{ac} - \frac{i}{2} \Gamma_{acr} \right) \\ -\gamma_{ba} & \hbar \omega - \varepsilon_{br} + \frac{i}{2} \Gamma_{br} & -\left( \gamma_{bc} - \frac{i}{2} \Gamma_{bcr} \right) \\ -\left( \gamma_{ca} - \frac{i}{2} \Gamma_{car} \right) & -\left( \gamma_{cb} - \frac{i}{2} \Gamma_{cbr} \right) & \hbar \omega - \varepsilon_{cr} + \frac{i}{2} \Gamma_{cr} \end{bmatrix},$$

or in Dyson equation form (self-energies $\Gamma_{rr'}^{(a)}$ and $\Gamma_{rr'}^{(b)}$ become evident):

$$G_{mnr}^{R}(\omega) = \left( \Omega - [\gamma] + \frac{i}{\hbar} \left( \Gamma_{rr'}^{(a)} + \Gamma_{rr'}^{(b)} \right) \right)^{-1},$$

where $\Omega$ is the retarded Green’s function.
Where the matrices $\Omega$, $[\gamma]$, $\Gamma_{acr}^{(a)}$ and $\Gamma_{acr}^{(b)}$ are given by:

$$
\Omega = \begin{bmatrix}
\varepsilon_{aa} & 0 & 0 \\
0 & \varepsilon_{bc} & 0 \\
0 & 0 & \varepsilon_{cc}
\end{bmatrix},
[\gamma] = \begin{bmatrix}
0 & \gamma_{ab} & \gamma_{ac} \\
\gamma_{ba} & 0 & \gamma_{bc} \\
\gamma_{ca} & \gamma_{cb} & 0
\end{bmatrix},
\Gamma_{acr}^{(a)} = \begin{bmatrix}
\Gamma^{(a)}_{acr} & 0 & 0 \\
0 & \Gamma^{(a)}_{acr} & 0 \\
0 & 0 & \Gamma^{(a)}_{acr}
\end{bmatrix},
\Gamma_{acr}^{(b)} = \begin{bmatrix}
0 & 0 & 0 \\
0 & \Gamma^{(b)}_{bc} & \Gamma^{(b)}_{bcr} \\
0 & \Gamma^{(b)}_{cbr} & \Gamma^{(b)}_{cr}
\end{bmatrix},
$$

and the renormalized energies in matrix $\Omega$ are defined according to:

$$
\tilde{\varepsilon}_{mn} = \varepsilon_{mn} + J_m \sigma_{acr}^{(c)} \langle S_m \rangle.
$$

(A5)

**Appendix B: Effective Spin-Spin Hamiltonian**

The effective spin $\frac{1}{2}$ Hamiltonian for a spin trimer is written in the following way:

$$
H_{\text{spin}} = J_{ab} S_a \cdot S_b + J_{ac} S_a \cdot S_c + J_{bc} S_b \cdot S_c,
$$

(B1)

where $J_{mn}$ is given according to [25] as:

$$
J_{mn} = \frac{J_m J_n}{2} \int \int \frac{G_{mn}^{(0)}(\epsilon)G_{mn}^{(0)}(\epsilon') - G_{mn}^{(1)}(\epsilon)G_{mn}^{(1)}(\epsilon') - G_{mn}^{(1)}(\epsilon)G_{mn}^{(1)}(\epsilon') + G_{mn}^{(1)}(\epsilon)G_{mn}^{(1)}(\epsilon')}{\hbar \omega - \epsilon + \epsilon'} \frac{d\epsilon}{2\pi} \frac{d\epsilon'}{2\pi}.
$$

(B2)

The spin dot products shown in Eq. (B1), can be expanded as a complete Hilbert space according to the following tensor products:

$$
S_a \cdot S_b = S_{ax} \otimes S_{bx} \otimes I_{2\times2} + S_{ay} \otimes S_{by} \otimes I_{2\times2} + S_{az} \otimes S_{bz} \otimes I_{2\times2}.
$$

(B3)

$$
S_b \cdot S_c = I_{2\times2} \otimes S_{bx} \otimes S_{cx} + I_{2\times2} \otimes S_{by} \otimes S_{cy} + I_{2\times2} \otimes S_{bz} \otimes S_{cz}.
$$

(B4)

$$
S_a \cdot S_c = S_{ax} \otimes I_{2\times2} \otimes S_{cx} + S_{ay} \otimes I_{2\times2} \otimes S_{cy} + S_{az} \otimes I_{2\times2} \otimes S_{cz}.
$$

(B5)

where the operators $S_{1x}$, $S_{1y}$ and $S_{1z}$ for a spin $\frac{1}{2}$ degree of freedom are given the well known $\sigma$ matrices.

$$
H_{\text{spin}} = \begin{bmatrix}
J_{+++} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & J_{++-} & 2J_{bc} & 0 & 2J_{ac} & 0 & 0 & 0 & 0 & 0 \\
0 & 2J_{bc} & J_{+++} & 0 & 2J_{ab} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & J_{---} & 0 & 2J_{ab} & 2J_{ac} & 0 & 0 & 0 \\
0 & 2J_{ac} & 2J_{ab} & 0 & J_{+++} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 2J_{ab} & 0 & J_{---} & 2J_{bc} & 0 & 0 & 0 \\
0 & 0 & 0 & 2J_{ac} & 0 & 2J_{bc} & J_{+++} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & J_{+++}
\end{bmatrix}.
$$

(B6)

The diagonal elements of the above Eq. are given by:

$$
J_{+++} = J_{ab} + J_{ac} + J_{bc},
J_{++-} = J_{ab} - J_{ac} - J_{bc},
J_{---} = -J_{ab} - J_{ac} + J_{bc},
J_{---} = -J_{ab} + J_{ac} - J_{bc}.
$$

Eq. B6, can be written as a block matrix of $2 \times 2$, $1 \times 1$, $1 \times 3$ (zeros) and $3 \times 1$ (zeros) matrices as elements:

$$
\mathbf{H}_{\text{spin}} = \begin{bmatrix}
J_{11} & 0_{1\times3} & 0_{1\times3} & 0 \\
0_{3\times1} & J_{22} & J_{23} & 0_{3\times1} \\
0_{3\times1} & J_{32} & J_{33} & 0_{3\times1} \\
0 & 0_{1\times3} & 0_{1\times3} & J_{44}
\end{bmatrix}.
$$

(B7)
The eigen-value problem, $|\mathbf{H}_{\text{spin}} - \lambda I_{8\times 8}| = 0$, proceeds as follows:

$$
|\mathbf{H}_{\text{spin}} - \lambda I_{8\times 8}| = \begin{bmatrix}
J_{11} & 0_{4\times 3} & 0_{4\times 3} & 0 \\
0_{4\times 1} & J_{22} & J_{23} & 0_{4\times 1} \\
0_{4\times 1} & 0_{4\times 1} & J_{32} & J_{33} \\
0 & 0 & 0 & J_{44}
\end{bmatrix} - \begin{bmatrix}
\lambda & 0_{4\times 3} & 0_{4\times 3} & 0 \\
0_{4\times 1} & \lambda I_{3\times 3} & 0_{4\times 1} & 0_{4\times 1} \\
0_{4\times 1} & 0_{4\times 1} & \lambda I_{3\times 3} & 0_{4\times 1} \\
0 & 0 & 0 & \lambda
\end{bmatrix} = 0,
$$

$$
= \begin{bmatrix}
J_{11} - \lambda & 0_{4\times 3} & 0_{4\times 3} & 0 \\
0_{4\times 1} & J_{22} - \lambda I_{3\times 3} & J_{23} & 0_{4\times 1} \\
0_{4\times 1} & 0_{4\times 1} & J_{32} & J_{33} - \lambda I_{3\times 3} \\
0 & 0 & 0 & J_{44} - \lambda
\end{bmatrix} = 0,
$$

$$
= (J_{11} - \lambda) \begin{bmatrix}
J_{22} - \lambda I_{3\times 3} \\
J_{32} \\
J_{33} - \lambda I_{3\times 3} \\
J_{44} - \lambda
\end{bmatrix} = 0,
$$

$$
= (J_{11} - \lambda) [(J_{22} - \lambda I_{3\times 3})(J_{33} - \lambda I_{3\times 3})(J_{44} - \lambda) - J_{23}J_{32}(J_{44} - \lambda)] = 0,
$$

$$
= (J_{11} - \lambda)(J_{44} - \lambda) \begin{bmatrix}
J_{22} - \lambda I_{3\times 3} \\
J_{32} \\
J_{33} - \lambda I_{3\times 3} \\
-J_{23}J_{32}
\end{bmatrix} = 0.
$$

(B8)

From Eq. B6, matrices $J_{22}, J_{33}, J_{23}$ and $J_{32}$ are given by:

$$
J_{22} = \begin{bmatrix}
J_{++} & 2J_{bc} & 0 \\
2J_{bc} & J_{--} & 0 \\
0 & 0 & J_{+-}
\end{bmatrix}, \hspace{1cm} J_{33} = \begin{bmatrix}
J_{++} & 0 & 0 \\
0 & J_{--} & 2J_{bc} \\
0 & 2J_{bc} & J_{+-}
\end{bmatrix}, \hspace{1cm} J_{23} = \begin{bmatrix}
2J_{ac} & 0 & 0 \\
2J_{ab} & 0 & 0 \\
0 & 2J_{ac} & 2J_{ac}
\end{bmatrix}, \hspace{1cm} J_{32} = \begin{bmatrix}
2J_{ac} & 2J_{ab} & 0 \\
2J_{ab} & 0 & 0 \\
0 & 0 & 2J_{ac}
\end{bmatrix}.
$$

(B9)

The term $J_{23}J_{32}$ in Eq. B8 can be further elaborated as follows:

$$
J_{23}J_{32} = \begin{bmatrix}
2J_{ac} & 0 & 0 \\
2J_{ac} & 0 & 0 \\
0 & 2J_{ac} & 2J_{ac}
\end{bmatrix} = \begin{bmatrix}
4J_{ac}^{2} & 4J_{ac}J_{ab} & 0 \\
4J_{ac}J_{ab} & 4J_{ab}^{2} & 0 \\
0 & 0 & 4(J_{ac}^{2} + J_{ab}^{2})
\end{bmatrix},
$$

(B10)

and the term $(J_{22} - \lambda I_{3\times 3})(J_{33} - \lambda I_{3\times 3})$ is given by:

$$
(J_{22} - \lambda I_{3\times 3})(J_{33} - \lambda I_{3\times 3}) = \begin{bmatrix}
J_{++} - \lambda & 2J_{bc} & 0 \\
2J_{bc} & J_{--} - \lambda & 0 \\
0 & 0 & J_{+-} - \lambda
\end{bmatrix} = \begin{bmatrix}
J_{++} - \lambda & 0 & 0 \\
0 & J_{--} - \lambda & 2J_{bc} \\
0 & 2J_{bc} & J_{+-} - \lambda
\end{bmatrix},
$$

(B11)

and replacing the latter and former result in Eq. B8, the eigen-value problem now reads:

$$
|\mathbf{H}_{\text{spin}} - \lambda I_{8\times 8}| = (J_{11} - \lambda)(J_{44} - \lambda) \begin{bmatrix}
\lambda & 4J_{ac}^{2} & 2J_{bc} (J_{++} - \lambda) - 4J_{ac}J_{ab} & 4J_{bc}^{2} \\
2J_{bc} (J_{++} - \lambda) & 0 & 0 & 0 \\
4J_{ac}J_{ab} & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{bmatrix} = 0
$$

(B12)
Eigen-values and associated Eigen-vectors corresponding to the Quartet and two non-degenerate Doublet states are given by:

\[
\mathcal{E}^{(1)}_{\text{spin}} = \mathcal{J}_{ab} + \mathcal{J}_{ac} + \mathcal{J}_{bc}; \quad |\phi_1\rangle = |↑↑↑\rangle \\
\mathcal{E}^{(2)}_{\text{spin}} = \mathcal{J}_{ab} + \mathcal{J}_{ac} + \mathcal{J}_{bc}; \quad |\phi_2\rangle = \frac{1}{\sqrt{3}} (|↑↑↓\rangle + |↑↓↓\rangle + |↓↑↑\rangle) \\
\mathcal{E}^{(3)}_{\text{spin}} = \mathcal{J}_{ab} + \mathcal{J}_{ac} + \mathcal{J}_{bc}; \quad |\phi_3\rangle = \frac{1}{\sqrt{3}} (|↑↓↓\rangle + |↓↑↑\rangle + |↓↓↑\rangle) \\
\mathcal{E}^{(4)}_{\text{spin}} = \mathcal{J}_{ab} + \mathcal{J}_{ac} + \mathcal{J}_{bc}; \quad |\phi_4\rangle = |↓↓↓\rangle
\]

Moreover, the aim in this context is to evaluate the spin expectation values of the form \(\langle S_m \rangle\), for \(m = a, b, c\), to then feed them into the retarded Green’s function given by Eq. (A3), or in the inverse retarded Green’s function given by Eq. (A2) in the spirit of the work we presented in [217]. To move forward in that department, we employ the definition of the thermal expectation value given by:

\[
\langle S_m \rangle = \frac{1}{Z_s} \text{Tr} \left[ e^{-\beta \mathcal{H}_{\text{spin}}} S_m \right], \quad (B14)
\]

where the operator \(S_{m\perp}\), is the projection of the total spin operator onto the Hilbert space of spin \(S_m\), and \(Z_s\) is the partition function of the spin sub-system. Additionally, to fully determine the formation of Quartet and Doublet states for the antiferromagnetic and ferromagnetic ordering case, we calculate the elements of the spin density matrix \(\rho_{\text{spin}}\) in a diagonal basis as follows:

\[
\rho_{\text{spin}} = \frac{e^{-\beta \mathcal{H}_{\text{spin}}}}{Z_s}, \quad (B15)
\]

where \(\mathcal{H}_{\text{spin}}\) is the Hamiltonian described in Eq. (B6) in diagonal basis.

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