

Understanding decoherence in molecular spin qudits

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Molecular nanomagnets are quantum spin systems potentially serving as qudits for future quantum technologies thanks to their many accessible low-energy states. At low temperatures, the primary source of error in these systems is pure dephasing, caused by their interactions with the bath of surrounding nuclear spins degrees of freedom. Most importantly, as the system's dimensionality grows going from qubits to qudits, the control and mitigation of decoherence become more challenging. Here, we analyze the characteristics of pure dephasing in molecular qudits under spin-echo sequences. We use a realistic description of their interaction with the bath, whose non-Markovian dynamics is accurately computed by the cluster correlation expansion technique. First, we show that the differences in the expectation values of the local spin operators on the eigenstates of the qudit are the source of decoherence in these systems. Indeed, we demonstrate that this is a necessary and sufficient condition to prevent the decay of coherence with time, also introducing a parameter to quantify the deviation from such ideal condition. We illustrate this with two paradigmatic systems: a single giant spin and a composite antiferromagnetic spin system. We then advance a proposal for optimized nanomagnets, identifying key ingredients for engineering robust qudits for quantum technologies.

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I. INTRODUCTION

Quantum computation is a milestone with the potential to revolutionize various fields, from materials design to the optimization of complex processes. The hardest challenge in achieving practical quantum advantage lies in mitigating noise-induced errors. Even the most mature platforms, such as those based on superconducting transmon qubits or trapped ions, belong to the category of noisy intermediate-scale quantum (NISQ) devices. These systems are constrained by limited relaxation (T_1) and dephasing (T_2) times, which restrict the number of quantum gates that can be reliably executed due to error accumulation. Consequently, minimizing the depth of quantum circuits is critical for implementing algorithms effectively on NISQ devices. For example, in quantum computation, different algorithms [1–3], such as the variational quantum eigensolver [4,5], have been proposed to address electronic structure problems. Despite significant efforts to minimize the resource requirements for implementing this algorithm [6–10], simulating challenging prototypical systems

remains out of reach. To overcome noise-related limitations and achieve fault-tolerant quantum computation, the implementation of quantum error correction (QEC) is necessary. The core principle of QEC is expanding the Hilbert space beyond the conventional two-dimensional space of a single *qubit*. This is achieved by replacing two-level qubits with more complex logical units composed of multiple physical qubits [11]. However, this approach is significantly limited by the large resource demands of multiqubit codes, particularly due to the necessity of nonlocal gates operating on distinct physical units, which makes QEC highly challenging [12]. This difficulty motivates the exploration of alternative paradigms for implementing QEC. One such approach involves expanding the Hilbert space by encoding the logical qubit into a multilevel physical system (*qudit*) [13–19]. Whether applied to QEC, quantum computation, or quantum simulation, one of the primary advantages of qudits over traditional qubits lies in their ability to reduce the number of distinct physical units and two-body gates required for operations. This is because certain quantum operations that necessitate multiple gates in qubit-based systems can often be executed with just a single gate in qudit-based systems [20,21]. As a result, qudits not only lower the overall gate count but also enhance computational efficiency, making them a promising alternative for scalable quantum information processing.

In this regard, molecular spin systems and more specifically molecular nanomagnets (MNMs), represent an attractive platform due to the presence of many low-energy spin states,

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both nuclear and electronic ones, which can be exploited to encode and process quantum information. Additionally, they can be efficiently controlled using electromagnetic pulses in the microwave or radio frequency range [22,23]. The availability of these additional degrees of freedom has recently led to the suggestion of encoding qubits with embedded QEC within single molecules [18,24,25]. From a chemical point of view, the easiest way to implement this concept is provided by a spin- S ion, characterized by $2S + 1$ states. Similarly, giant-spin nanomagnets offer an analogous configuration, as their low-energy spectrum effectively maps onto an effective spin- S system. Increasing the value of S expands the number of energy levels that can be exploited.

However, this expansion in computational space comes with greater challenges in controlling decoherence. As the system's dimensionality grows, interactions with the surrounding nuclear bath lead to greater susceptibility to noise and errors. To try to overcome this problem, many strategies have been developed lately. For example, a general dynamical decoupling framework tailored for qudits was lately developed [26] and tested for the case of superconducting transmon circuits.

In the field of molecular magnetism, in recent years, significant efforts have been devoted to understanding and mitigating decoherence effects in MNMs [27–29]. For example, hydrogen-free environments have been designed [30] to eliminate the effects of fluctuating proton spins, leading to remarkable improvements in coherence times [31]. Another complementary strategy is to optimize the choice of spin eigenstates encoding quantum information, making them as resilient as possible to the effects of the surrounding bath. Ideally, if these states spanned a decoherence-free subspace (DFS) [32], they would be inherently immune to decoherence effects. Yet, a generic bath will dipolarly couple to the full set of molecular spin operators ($3N$, N being the number of spins), preventing a strict realization of DFS conditions. Nevertheless, when the eigenstates are well separated relative to the dipolar interaction scale, significant opportunities for decoherence mitigation remain. For example, a pair of qubit states in a clock-transition condition has decoherence suppressed to first-order in the qubit-bath interaction. This clock condition is achieved by carefully selecting states with specific symmetries or properties (e.g., anticrossings in the field-dependence of molecular states [33–35]).

It is important to note that while for a qubit the long T_2 time refers to a single, specific pair of eigenstates, a practical implementation of a d -dimensional molecular qudit requires long T_2 times for superpositions of all $\binom{d}{2}$ pairs of eigenstates. This makes it significantly more challenging to identify optimal setups for mitigating decoherence. In this paper, we analyze the characteristics of decoherence using a realistic description of molecular qudits and the bath, whose non-Markovian dynamics is accurately computed using a cluster correlation expansion.

In Sec. II, we show how to model the molecular systems of interest through a spin Hamiltonian approach in a perturbation theory framework. In Sec. III, we introduce the technique used to compute the dynamics of the spins. In Sec. IV, we develop a microscopic model of decoherence for molecular spin systems undergoing pure dephasing under a control sequence of

π -pulses, including the Hahn echo [36] and the Carr-Purcell-Meiboom-Gill sequence [37,38]. We demonstrate a necessary and sufficient condition to prevent the decay of coherence with time. Moreover, we introduce a parameter to quantify the deviation from this ideal condition. We show that for a coherent superposition of a pair of eigenstates, the key factor driving decoherence is the difference in the expectation values of *local* spin operators between the two states, and not of *total* ones, as one could guess. Thus, minimizing these differences can enhance the coherence time of the superposition.

In Sec. V, we illustrate this concept using two paradigmatic systems. The first one is a single giant spin $S = 10$ highlighting the impact that even tiny differences in the expectation values of spin operators have on the decay of coherence. The second one consists of a composite system containing five spins $S_i = 1/2$ ($i = 1, \dots, 5$), with competing, antiferromagnetic (AFM) interactions. It allows us to show the importance of the expectation values of local spin operators over total spin operators in qudits made of several magnetic centers. By exploiting the knowledge gained through the aforementioned cases, and accordingly with the experimental constraints, we advance the proposal for a qudit that leverages the properties of the introduced systems. These results allow us to identify which are the ingredients that can be controlled to engineer optimal molecular qudits for different applications in quantum technologies. Finally, our method is completely general and can be applied to other spin-based quantum systems.

II. THEORETICAL BACKGROUND

A. Model Hamiltonian

The spin Hamiltonian describing the problem of a central system of spins interacting with a spin bath can be written as follows:

$$H = H_S + H_B + H_{SB}, \quad (1)$$

where H_S is the Hamiltonian of the central system, H_B describes the intrinsic bath interactions, and H_{SB} accounts for the interactions between each element belonging to the central system and the spins contained in the bath. The central system Hamiltonian has the form

$$H_S = \sum_i \mathbf{B} \cdot \boldsymbol{\Gamma}^i \cdot \mathbf{S}_i + \sum_{i,j} \mathbf{S}_i \cdot \mathbf{D}^{ij} \cdot \mathbf{S}_j, \quad (2)$$

where $\mathbf{S}_i$ is the i th system spin coupled to the external magnetic field $\mathbf{B}$ through the gyromagnetic ratio tensor $\boldsymbol{\Gamma}^i$, whereas $\mathbf{D}^{ij}$ is the tensor describing the interactions between the spin pair (i, j) within the system. If $i = j$, $\mathbf{D}$ denotes the self-interaction tensor, i.e., the zero-field splitting tensor or the quadrupole tensor in the case of electronic and nuclear spins, respectively. The intrinsic Hamiltonian of the bath is

$$H_B = \sum_i \mathbf{B} \cdot \boldsymbol{\gamma}^i \cdot \mathbf{I}_i + \sum_{i,j} \mathbf{I}_i \cdot \mathbf{J}^{ij} \cdot \mathbf{I}_j. \quad (3)$$

Similarly to the previous case, $\mathbf{I}_i$ represents the i th bath spin coupled to the external magnetic field $\mathbf{B}$ through the gyromagnetic ratio tensor $\boldsymbol{\gamma}^i$, whereas $\mathbf{J}^{ij}$ is the interaction tensor bath spins belonging to the pair (i, j) . The case $i = j$ describes the quadrupolar interaction. If $i \neq j$, we assume the two nuclei

interacting via magnetic dipole-dipole interaction. In the point dipole approximation, it reads

$$\mathbf{J}^{ij} = \frac{\mu_0}{4\pi |\mathbf{R}_{ij}|^3} \left(\boldsymbol{\gamma}^i \cdot \boldsymbol{\gamma}^j - 3 \frac{\boldsymbol{\gamma}^i \cdot \mathbf{R}_{ij} \otimes \boldsymbol{\gamma}^j \cdot \mathbf{R}_{ij}}{|\mathbf{R}_{ij}|^2} \right), \quad i \neq j, \quad (4)$$

where μ_0 is the magnetic permeability of free space and $\mathbf{R}_{ij}$ is the distance vector between the involved spins i and j located, respectively, in position $\mathbf{R}_i$ and $\mathbf{R}_j$. The system-bath Hamiltonian H_{SB} can be expressed as

$$H_{SB} = \sum_{i,j} \mathbf{S}_i \cdot \mathbf{A}^{ij} \cdot \mathbf{I}_j, \quad (5)$$

where $\mathbf{A}^{ij}$ denotes the interaction tensor between the i th spin belonging to the central system and the j th spin contained in the bath. Once again, a dipole-dipole interaction is assumed:

$$\mathbf{A}^{ij} = \frac{\mu_0}{4\pi |\mathbf{R}_{ij}|^3} \left(\boldsymbol{\Gamma}^i \cdot \boldsymbol{\gamma}^j - 3 \frac{\boldsymbol{\Gamma}^i \cdot \mathbf{R}_{ij} \otimes \boldsymbol{\gamma}^j \cdot \mathbf{R}_{ij}}{|\mathbf{R}_{ij}|^2} \right), \quad (6)$$

with $\mathbf{R}_{ij}$ being the vector connecting the system spin i and the bath spin j . It is worth to note that the methods and results discussed in this paper can be straightforwardly extended to a more general form of $\mathbf{A}^{ij}$.

In this framework, the total Hamiltonian (1) is defined in the Hilbert space $\mathcal{H} = \mathcal{H}_S \otimes \mathcal{H}_B$, where $\mathcal{H}_S$ is the Hilbert space associated with the system, and $\mathcal{H}_B$ the one related to the bath. A basis set for $\mathcal{H}$ is given by the kets $|\psi\phi\rangle \equiv |\psi\rangle \otimes |\phi\rangle$, where $|\psi\rangle$ and $|\phi\rangle$ are the eigenstates of H_S and H_B , respectively. Labeling the eigenvalues of H_S as E_S^ψ , the total Hamiltonian may be put in matrix form

$$\begin{aligned} \langle \psi' \phi' | H | \psi \phi \rangle &= \delta_{\psi' \psi} \delta_{\phi' \phi} E_S^\psi + \delta_{\psi' \psi} \langle \psi' \phi' | H_B + H_{SB} | \psi \phi \rangle \\ &+ (1 - \delta_{\psi' \psi}) \langle \psi' \phi' | H_{SB} | \psi \phi \rangle, \end{aligned} \quad (7)$$

where the first term is diagonal in $\mathcal{H}$ and the second one collects all the terms of the system-bath coupling that are diagonal in $\mathcal{H}_S$ together with the ones of the bath Hamiltonian. The third term involves states with different ψ in the H_{SB} interaction (off-diagonal elements), which make the treatment of the problem more troublesome. To address this, we apply a canonical transformation to reduce the magnitude of the matrix elements of H_{SB} that couple states with different ψ . Given that the systems of interest have H_S as the dominant component of the Hamiltonian compared to H_{SB} , we adopt a perturbative approach, assuming the dipolar coupling $\mathbf{A}$ as a perturbative parameter [see Eq. (5)]. The application of the canonical, perturbative Schrieffer-Wolff transformation [39–41], yields a unitary transformed Hamiltonian where the off-diagonal terms are much smaller than the original ones. By neglecting these elements, we finally obtain the following effective Hamiltonian for the bath, conditioned on the system being in the state $|\psi\rangle$:

$$H^\psi = E_S^\psi \mathbb{1} + H_B + H_{SB1}^\psi + H_{SB2}^\psi, \quad (8)$$

$\mathbb{1}$ being the identity operator in the $\mathcal{H}_B$ Hilbert space. H_{SB1} and H_{SB2} are the central system-bath interaction terms treated at first and second order in perturbation theory, respectively.

They have the following form:

$$H_{SB1}^\psi = \sum_{i,j} \langle \psi | \mathbf{S}_i | \psi \rangle \cdot \mathbf{A}^{ij} \cdot \mathbf{I}_j \quad (9)$$

and

$$H_{SB2}^\psi = \sum_{j,l} \mathbf{I}_j \cdot \mathbf{T}^{jl}(\psi) \cdot \mathbf{I}_l,$$

where

$$\mathbf{T}^{jl}(\psi) = \sum_{\psi', i, k} \frac{\langle \psi | \mathbf{S}_i | \psi' \rangle \cdot \mathbf{A}^{ij} \otimes \langle \psi' | \mathbf{S}_k | \psi \rangle \cdot \mathbf{A}^{kl}}{E_{\psi'} - E_{\psi}}. \quad (10)$$

It is important to stress that both Eqs. (9) and (10) depend on the specific state $|\psi\rangle$ of the central system. This aspect will be crucial in the description of the temporal dynamics of a coherent superposition of central system states, as it will be extensively discussed in the following.

B. Decoherence

At low temperatures (≈ 1 K or below), the main source of decoherence for MNMs is represented by the coupling of the central system with the surrounding spin bath. Indeed, in this regime, the contribution to decoherence due to the interactions with phonons is usually negligible. Moreover, many experiments on molecular spin complexes have shown that the relaxation time T_1 becomes several orders of magnitude longer than the dephasing time [42–44]. Therefore, within the timescale we are interested in, the state populations (i.e., the diagonal terms of its density matrix) do not change in time. Here, we want to model how an arbitrary qubit subspace within a larger qudit Hilbert space is affected by pure dephasing due to the system-bath interaction. Thus, we consider the initial density matrix for the overall system (central system + bath) $|\psi\rangle_{\alpha, \beta} \langle \psi|_{\alpha, \beta} \otimes \rho_B$, where ρ_B is the initial density matrix of the bath and

$$|\psi\rangle_{\alpha, \beta} = C_\alpha |\alpha\rangle + C_\beta |\beta\rangle \quad (11)$$

is the initial state of the system, prepared in a superposition between the two eigenstates $|\alpha\rangle$ and $|\beta\rangle$ of Eq. (2) with coefficients C_α and C_β . The whole density matrix evolves in time according to the von-Neumann equation through the Hamiltonian $\bigoplus_\psi H^\psi$, block diagonal in $\mathcal{H}$ and with H^ψ defined in Eq. (8). Due to the entanglement between the system and the bath, after a time τ , the coherence term of the reduced density matrix for the system will be

$$C_\alpha C_\beta^* \text{tr}_B(e^{-iH^\alpha t} \rho_B e^{iH^\beta t}), \quad (12)$$

where $t = \tau/\hbar$ and $\hbar$ is the reduced Planck's constant. Note that this is the only nontrivial coherence term in the reduced density matrix because we considered a superposition of two eigenstates and no population decay to other states is admitted in the model. Now, we define the coherence factor as the ratio between the final and the initial coherence, that is,

$$L^{\alpha\beta}(t) = \text{tr}_B(e^{iH^\beta t} e^{-iH^\alpha t} \rho_B) \quad (13)$$

with the initial condition $L^{\alpha\beta}(0) = 1$ because, at $t = 0$, the coherence is $C_\alpha C_\beta^*$. To recover the central system coherence

factor loss over time, a powerful approach known as dynamical decoupling was developed [45,46]. The key idea is to effectively decouple the central spin from the environment by frequently flipping the central system spin through a series of electromagnetic pulses. Indeed, this procedure allows us to switch H^α and H^β during the time propagation, partially compensating the pure dephasing induced by these Hamiltonians. Therefore, Eq. (13) can be generalized by supposing the application of a set of instantaneous π -pulses on the system that swaps the probability amplitude of the states α and β . The time evolution operators related to the application of k π -pulses are

$$U^{\alpha(\beta)}(t) = \begin{cases} e^{-iH^{\alpha(\beta)}\Delta t_1}, & k = 0, \\ \prod_{j=1}^k e^{-iH^{\beta(\alpha)}\Delta t_j} e^{-iH^{\alpha(\beta)}\Delta t_j}, & k > 0, \end{cases} \quad (14)$$

where $\Delta t_j = t_j - 2 \sum_{l=1}^j \Delta t_{l-1}$, with $\Delta t_0 = 0$ and $t \in \mathbb{R}^k$, specifies the free evolution time before and after the j th π -pulse $\forall j > 1$. From a physical viewpoint, if $k = 0$ (i.e., no electromagnetic pulses are applied), the system undergoes a free induction decay, whereas $k = 1$ implies the use of the Hahn echo technique and, for $k > 1$, the CPMG pulse sequence is represented. In this general framework, the coherence factor assumes the following form:

$$L^{\alpha\beta}(t) = \text{tr}_B(U^\beta(t)^\dagger U^\alpha(t)\rho_B) \quad (15)$$

and its square modulus is the quantity we want to preserve. Note that we assumed neither that ρ_B is thermal at each time, nor a Markovian dynamics for the system, thus the resulting process cannot be described in terms of Lindblad master Eqs. [47,48].

III. METHODS

To calculate the coherence factor defined in Eq. (15), it is necessary to evaluate the time propagators for the bath. However, even for small baths, it is impossible to numerically carry out this task due to the exponential growth of the computational costs. To this end, we resorted to the cluster correlation expansion (CCE) approach [49–51], which allows one to approximate the coherence factor with its product expansion truncated at a certain order. More specifically, this technique represents a systematic method to take into account the many-body correlations in the bath, order by order. By considering a Hamiltonian diagonal in the system Hilbert space, like the one in Eq. (8), we define first of all the coherence factor given by a certain cluster C belonging to the bath as

$$L_C^{\alpha\beta}(t) = \text{tr}(U_C^\beta(t)^\dagger U_C^\alpha(t)\rho_B), \quad (16)$$

where $U_C^{\alpha(\beta)}(t)$ is the propagator for the cluster C . This is obtained by substituting the Hamiltonian $H^{\alpha(\beta)}$ in the exponential of Eq. (14) with the one associated with the cluster C , so replacing all the operator I_i in $H^{\alpha(\beta)}$ $\forall i \notin C$ with their mean-field average. The coherence factor (15) can be expanded as

$$L^{\alpha\beta}(t) = \prod_C \tilde{L}_C^{\alpha\beta}(t), \quad (17)$$

where C runs over all the possible clusters contained in the spin bath. The cluster correlations are recursively defined as

$$\tilde{L}_C^{\alpha\beta}(t) = \frac{L_C^{\alpha\beta}(t)}{\prod_{\tilde{C} \subset C} \tilde{L}_{\tilde{C}}^{\alpha\beta}(t)}, \quad (18)$$

where $\tilde{C} \subset C$. For example, to evaluate the coherence factor term

$$\tilde{L}_{\{i,j\}}^{\alpha\beta}(t) = \frac{L_{\{i,j\}}^{\alpha\beta}(t)}{\tilde{L}_0^{\alpha\beta}(t) \tilde{L}_{\{i\}}^{\alpha\beta}(t) \tilde{L}_{\{j\}}^{\alpha\beta}(t)} \quad (19)$$

associated with the cluster $\{i, j\}$, where i, j are two bath spins, we need to evaluate the following terms of the expansion:

$$\begin{aligned} \tilde{L}_0^{\alpha\beta}(t) &= L_0^{\alpha\beta}(t) \in \mathbb{C}, \\ \tilde{L}_{\{i\}}^{\alpha\beta}(t) &= L_{\{i\}}^{\alpha\beta}(t) / \tilde{L}_0^{\alpha\beta}(t), \\ \tilde{L}_{\{j\}}^{\alpha\beta}(t) &= L_{\{j\}}^{\alpha\beta}(t) / \tilde{L}_0^{\alpha\beta}(t). \end{aligned} \quad (20)$$

The CCE theory is related to the linked cluster expansion (LCE) [52,53]. Indeed, the LCE approach for qubit decoherence has been developed for bath spins with $S > 1/2$ and $S = 1/2$, respectively, in Refs. [49,54], showing that

$$\tilde{L}_C = e^{\pi(C)}, \quad (21)$$

where $\pi(C)$ is the sum of all the connected Feynman diagrams in which all and only the spins in C underwent a flip-flop transition, demonstrating that $\tilde{L}_C$ is a summation of infinite diagrams.

For all the molecular systems considered below, the expansion in Eq. (17) has been truncated to its second order (2-CCE):

$$L^{\alpha\beta}(t) \approx \tilde{L}_0^{\alpha\beta}(t) \prod_i \tilde{L}_{\{i\}}^{\alpha\beta}(t) \prod_{i,j} \tilde{L}_{\{i,j\}}^{\alpha\beta}(t). \quad (22)$$

Indeed, within the timescale considered, we have verified that spin clusters containing two elements are sufficient to cause complete decoherence, leading to convergence in the CCE. This order of convergence in the expansion is in agreement with other results in the literature, where the CCE method is applied to molecular spin systems [55,56]. An open-source Python package [57] that implements the CCE theory for a central system of spins undergoing environment-induced decoherence is already available. Nevertheless, in order to meet the specific needs of our study, we developed from scratch tailored code.

Equipped with a model to describe decoherence and a method to properly simulate the behavior of a many-body bath, we proceed by defining a strategy to counteract decoherence itself.

IV. THEORETICAL RESULTS

In the present section, we will prove a necessary and sufficient condition on the Hamiltonian operators H^α and H^β to keep the coherence factor $L^{\alpha\beta}(t)$ equal to 1. Moreover, we will show with analytical arguments that this condition can be expressed in terms of differences in expectation values of its local spin operators.

A. Hamiltonian and decoherence

In this subsection, we will prove that $L^{\alpha\beta}(t) = 1$ for each bath reduced density matrix ρ_B , $\forall k \geq 1$ and $\forall t$ if and only if

$$[H^\alpha, H^\beta] = 0. \quad (23)$$

First of all, we will prove the *only if* implication. We start by writing the condition $L^{\alpha\beta}(t) = 1$ as

$$\text{tr}_B([U^\beta(t)^\dagger U^\alpha(t) - \mathbb{1}]\rho_B) = 0, \quad (24)$$

where we used the fact that $\text{tr}_B(\rho_B) = 1$. Since the Hilbert-Schmidt inner product between the term in the square brackets and ρ_B must be 0 for each ρ_B , we find that

$$U^\beta(t)^\dagger U^\alpha(t) = \mathbb{1} \quad (25)$$

that can be written as

$$\prod_{l=1}^k e^{iH^\beta \Delta t_{k-l+1}} e^{iH^\alpha \Delta t_{k-l+1}} \prod_{m=1}^k e^{-iH^\beta \Delta t_m} e^{-iH^\alpha \Delta t_m} = \mathbb{1}. \quad (26)$$

Because of the independence of the Δt_l variables, we can write

$$\begin{aligned} M &= e^{-iH^\alpha \Delta t_1} e^{-iH^\beta \Delta t_1} e^{iH^\alpha \Delta t_1} e^{iH^\beta \Delta t_1} \\ &= e^{-i\Delta t_1(H^\alpha + H^\beta) - \Delta t_1^2/2[H^\alpha, H^\beta]} \\ &\quad + \dots e^{+i\Delta t_1(H^\alpha + H^\beta) - \Delta t_1^2/2[H^\alpha, H^\beta] + \dots} \\ &= e^{\sum_{n=2}^{\infty} \Delta t_1^n f_n(H^\alpha, H^\beta)}, \end{aligned} \quad (27)$$

where the matrix M does not depend on any variable and $f_n(H^\alpha, H^\beta)$ are functions of the Hamiltonians obtained using the well-known Baker-Campbell-Hausdorff formula. Since M is constant for each $\Delta t_1 \in \mathbb{R}$, we must have that $f_n(H^\alpha, H^\beta) = 0 \quad \forall n$, thus $M = \mathbb{1}$. For $n = 2$, we note that $f_2(H^\alpha, H^\beta) = -\Delta t_1^2/2[H^\alpha, H^\beta]$, then this condition is fulfilled only if $[H^\alpha, H^\beta] = 0$. Since, by definition, we know that also the other terms $f_n(H^\alpha, H^\beta)$ are zero if $[H^\alpha, H^\beta] = 0$, then we demonstrated our claim. Now, the *if* implication can be easily proved. Indeed, by supposing that $[H^\alpha, H^\beta] = 0$ is true, from Eq. (27), we get that $M = 1$ because $f_n(H^\alpha, H^\beta) = 0 \quad \forall n$, as outlined above. Thus, we satisfied Eq. (26), obtaining that $L^{\alpha\beta}(t) = 1$.

Thus, we showed the bijective relation between the coherence factor and the commutation of the Hamiltonian operators. Note that, since $M = \mathbb{1}$, the coherence factor is preserved after each pulse $j = 1, \dots, k$ because, as we assumed in Eq. (14), the free propagation before and after the pulse is the same.

B. Decoherence and expectation values of local spin operators

The content of this subsection is dedicated to the demonstration of the connection between the coherence factor and the expectation values of its local spin operators starting from Eq. (23). By taking into account the Hamiltonian in Eq. (8), we can write the commutator of two Hamiltonian operators,

conditioned on the states $|\alpha\rangle$ and $|\beta\rangle$, as

$$\begin{aligned} [H^\alpha, H^\beta] &= [H_{SB1}^\alpha, H_{SB1}^\beta] + [H_B, \Delta H_{SB1}] \\ &\quad + [H_B, \Delta H_{SB2}] + [H_{SB1}^\alpha, H_{SB2}^\beta] \\ &\quad + [H_{SB2}^\alpha, H_{SB1}^\beta] + [H_{SB2}^\alpha, H_{SB2}^\beta], \end{aligned} \quad (28)$$

where $\Delta H_{SB1(2)} = H_{SB1(2)}^\beta - H_{SB1(2)}^\alpha$. The first term on the right-hand side can be written as

$$\begin{aligned} [H_{SB1}^\alpha, H_{SB1}^\beta] &= \sum_{\substack{k,l,j \\ \mu,v,\zeta,\delta,\theta}} i \langle \beta | S_k^\mu | \beta \rangle \langle \alpha | S_l^\zeta | \alpha \rangle A_{\mu\nu}^{kj} A_{\zeta\delta}^{lj} \epsilon_{v\delta\theta} I_j^\theta \\ &= \sum_{\substack{k,l,j \\ \mu,v,\zeta,\delta,\theta}} \frac{i}{2} (\langle \beta | S_k^\mu | \beta \rangle - \langle \alpha | S_k^\mu | \alpha \rangle) \\ &\quad \times (\langle \beta | S_l^\zeta | \beta \rangle + \langle \alpha | S_l^\zeta | \alpha \rangle) A_{\mu\nu}^{kj} A_{\zeta\delta}^{lj} \epsilon_{v\delta\theta} I_j^\theta, \end{aligned} \quad (29)$$

where k and l span over the central system spins, j refers to a bath spin, whereas $\mu, \zeta, v, \delta, \theta = x, y, z$ and $\epsilon_{v\delta\theta}$ is the Levi-Civita tensor. For the second one, we get

$$[H_B, \Delta H_{SB1}] = \sum_{\substack{k,j \\ \mu,v}} (\langle \beta | S_k^\mu | \beta \rangle - \langle \alpha | S_k^\mu | \alpha \rangle) A_{\mu\nu}^{kj} [H_B, I_j^v], \quad (30)$$

and Eq. (28) becomes

$$\begin{aligned} [H^\alpha, H^\beta] &= \sum_{\substack{k,l,j \\ \mu,v,\zeta,\delta,\theta}} (\langle \beta | S_k^\mu | \beta \rangle - \langle \alpha | S_k^\mu | \alpha \rangle) \Gamma_{\eta\mu}^k \tilde{A}_{\eta\nu}^{kj} \\ &\quad \times \left((\langle \beta | S_l^\zeta | \beta \rangle + \langle \alpha | S_l^\zeta | \alpha \rangle) \frac{i}{2} A_{\zeta\delta}^{lj} \epsilon_{v\delta\theta} I_j^\theta + [H_B, I_j^v] \right) + \tilde{R}, \end{aligned} \quad (31)$$

where, again, k, l, j refer to specific spins, $\mu, \eta, \zeta, v, \delta, \theta = x, y, z$ and

$$\tilde{A}^{kj} = \frac{\mu_0}{4\pi |\mathbf{R}_{kj}|^3} \left(\boldsymbol{\gamma}^j - 3 \frac{\mathbf{R}_{kj} \otimes \boldsymbol{\gamma}^j \cdot \mathbf{R}_{kj}}{|\mathbf{R}_{kj}|^2} \right). \quad (32)$$

In Eq. (31), the operator $\tilde{R}$ includes all the commutators, appearing in Eq. (28), containing the terms $H_{SB2}^{\alpha(\beta)}$ at least once. In Appendix A, we will show that, under the proper hypothesis, $\tilde{R}$ can be neglected. If that is the case, we get

$$[H^\alpha, H^\beta] \approx \sum_{k,\mu,\eta} (\langle \beta | S_k^\mu | \beta \rangle - \langle \alpha | S_k^\mu | \alpha \rangle) \Gamma_{\eta\mu}^k O_{\eta}^k, \quad (33)$$

where $\Gamma_{\eta\mu}^k$ represents the central system gyromagnetic ratio tensor, whereas the set of O_{η}^k operators gathers together all the terms in Eq. (31) that have not been explicitly isolated. Note that these operators contain all the information involving the nuclear spin bath parameters, including the relative distances between the system and bath spins, which cannot be controlled since we are outlining a strategy to engineer the system only. Equation (33) allows us to isolate and highlight the key ingredients affecting the coherence dynamics that depend uniquely on the central system. They all appear in the form of differences between expectation values of *local*

spin operators, which are strictly related to the structure of the eigenstates $|\alpha\rangle$ and $|\beta\rangle$. By acting on them, we aim to reduce the value of the commutator between the Hamiltonians to approach condition (23) and, therefore, to increase the correlation factor. To this purpose, we define $W_k = \{i : \mathbf{R}_i \equiv \mathbf{R}_k\}$, the equivalence class of spins of the system that share the same spatial position of the spin k . Indeed, each class can contain up to two elements in the case of a nuclear spin and the electron associated with it. It follows that Eq. (33) satisfies relation (23) if

$$\sum_{\substack{i \in W_k \\ \mu}} \langle \beta | S_i^\mu | \beta \rangle \Gamma_{\eta\mu}^i = \sum_{\substack{i \in W_k \\ \mu}} \langle \alpha | S_i^\mu | \alpha \rangle \Gamma_{\eta\mu}^i, \quad \forall \eta, W_k. \quad (34)$$

From a physical viewpoint, this means that, if the expectation values of the spin operators on $|\alpha\rangle$ and $|\beta\rangle$ are the same for each spatial direction η and site equivalence class W_k , the evolution in time of the bath under the two Hamiltonians generated by the pulses is the same. If $\Gamma_{\eta\mu}^i = \delta_{\eta\mu} \Gamma_\eta^i$ and the system spins are located in different spatial positions, we get the following equation, which offers a clearer physical interpretation:

$$\langle \beta | S_k^\eta | \beta \rangle = \langle \alpha | S_k^\eta | \alpha \rangle, \quad \forall k, \eta. \quad (35)$$

Thus, in this case, condition (23) is fulfilled if the expectation values of the *local* spin operators, when evaluated over the two system eigenstates combined in the initial coherent superposition reported in Eq. (11), are exactly the same. In principle, all the spatial components of the spin operators S_k should be considered. In practice, in systems like the ones that we will show in the following, where the leading interaction is represented by the Zeeman term [first term at second member in Eq. (2)], only the component (z) parallel to the external field is relevant. The closer we are to the ideal conditions expressed in Eq. (34) or (35), the less the bath can distinguish the order in which the propagators associated with H^α and H^β are applied. As a result, the Hilbert space generated by $|\alpha\rangle$ and $|\beta\rangle$ effectively behaves as a decoherence-free subspace [58], in agreement with the specific result shown in Ref. [59] (more details in the Supplemental Material [60]). Moreover, since $|\alpha\rangle$ and $|\beta\rangle$ are eigenstates, the decoherence cannot emerge from the dynamics due to the system Hamiltonian [61]. In the case of qubits, by encoding information in two eigenstates that undergo an anticrossing at a specific applied field, one realizes clock-transition conditions [33]. The transition frequency between the two levels becomes first order insensitive to small fluctuations in the magnetic field, and both levels exhibit equal magnetization:

$$\sum_k \Gamma_z^k \langle \beta | S_k^z | \beta \rangle = \sum_k \Gamma_z^k \langle \alpha | S_k^z | \alpha \rangle. \quad (36)$$

This condition can imply Eq. (35), for instance, through symmetry arguments, but not necessarily. The most favorable condition is when the clock transition occurs at zero applied field, as in this case time-reversal symmetry enforces $\langle \alpha | S_k^z | \alpha \rangle = \langle \beta | S_k^z | \beta \rangle = 0 \forall k$.

For qudits, the challenge lies in the relevance of multiple transition frequencies, making it extremely difficult to satisfy condition (36) for all of them-except at zero applied field. This would require a non-Kramers nanomagnet (with

an even number of electrons) that possesses sufficiently low symmetry, ensuring the presence of d low-lying nonmagnetic singlet eigenstates. These states must exhibit well-spaced energy gaps of similar magnitude to remain within an addressable energy window compatible with available magnetic pulses. Additionally, effective pulse operations require sizable magnetic-dipole matrix elements between multiple pairs of states. Finally, no energy gap should be so small that second-order decoherence contributions become significant.

Meeting all these constraints in a single physical system is highly challenging, particularly because the zero-field requirement precludes any external control over the Hamiltonian. Therefore, rather than aiming for a perfectly optimal control of decoherence, we will explore whether suboptimal but still viable conditions can be achieved in realistic systems and experimental setups, and whether for such systems, the effect of second-order terms in decoherence is actually minor. We stress that we do not require Markovian dynamics [62] because we only need the applicability of the Schrieffer-Wolff transformation for the eigenstates of interest, extending the range of applicability of our method.

V. NUMERICAL RESULTS

In this section, we illustrate the impact on the coherence factor when the ideal condition expressed in Eq. (34) is not met, using two representative case studies. Additionally, we present an example of a realistic molecular spin qudit.

For this purpose, we define the following parameter:

$$\Delta = \sum_{\substack{W_k \\ \eta}} \left| \sum_{\substack{i \in W_k \\ \mu}} \Gamma_{\eta\mu}^i (\langle \beta | S_i^\mu | \beta \rangle - \langle \alpha | S_i^\mu | \alpha \rangle) \right| \quad (37)$$

that measures how far we are from the ideal condition expressed in Eq. (23). Note that, in the following, we will study central systems made of electronic spins only. In addition, we suppose diagonal gyromagnetic ratio tensors. It follows that, considering Eq. (35), Eq. (37) takes the following simplified form:

$$\Delta = \sum_{k,\eta} |\Gamma_{\eta\eta}^k (\langle \beta | S_k^\eta | \beta \rangle - \langle \alpha | S_k^\eta | \alpha \rangle)|. \quad (38)$$

All the numerical values of Δ reported in this work will be expressed in Bohr magneton units. In all the systems we considered, a Hanh echo pulse sequence has been considered to suppress the trivial effect of the free induction decay, modeled as explained in Sec. II B. Besides, the randomly generated spin baths are composed of 1000 nuclear spins ($I = 1/2$) distributed into a spherical volume of radius 20 Å, with the only constraint of setting the minimum distance between each pair of spins (belonging to the system or the bath) to a typical value of 3 Å.

A. Single giant spin- S system

As a first example, we report the case of the simplest molecular spin qudit, namely, a system that contains a single spin $S > 1/2$. Specifically, we consider a giant electronic spin with $S = 10$, which provides a large set of states for potential

logical encoding. Note that there are no real representatives of single ions with an electronic spin $S = 10$. However, there are many examples of molecular clusters composed of many strongly interacting metal ions, whose spins are locked at low temperatures into an effective “giant spin.” In these cases, such as the well-known Mn_{12} and Fe_8 MNMs [63,64], the giant spin describes the whole magnetic core of the molecule, and within the ground multiplet local spin operators are all proportional to the total spin operators $\mathbf{S}_k = A_k \mathbf{S}$. Thus, the low-energy Hamiltonian and Eq. (38) can be formulated in terms of the total spin only. Given the illustrative purpose of the present example, to maintain simplicity and avoid specifying the internal spin structure of any particular MNM, we assume k -independent values for $\Gamma_{\eta\eta}^k$ and projection coefficients A_k (i.e., $A_k = S/N_s$, N_s being the number of ions). Thus, Eq. (38) can be expressed solely in terms of the total spin. The effective Hamiltonian has the form

$$H_S = \mathbf{S} \cdot \mathbf{D}_{\text{ZFS}} \cdot \mathbf{S} + \mathbf{B} \cdot \mathbf{\Gamma} \cdot \mathbf{S}, \quad (39)$$

where $\mathbf{D}_{\text{ZFS}}$ is the zero field splitting tensor, $\mathbf{B}$ is the external magnetic field vector, and $\mathbf{\Gamma}$ is the gyromagnetic ratio tensor. $\mathbf{D}_{\text{ZFS}}$ can be written as

$$\mathbf{D}_{\text{ZFS}} = \begin{pmatrix} -D/3 + E & 0 & 0 \\ 0 & -D/3 - E & 0 \\ 0 & 0 & 2D/3 \end{pmatrix},$$

where D and E are defined starting from the initial components of the tensor $D_{\text{ZFS}}^{xx}, D_{\text{ZFS}}^{yy}, D_{\text{ZFS}}^{zz}$, referred to the x, y, z coordinate axes: $D = D_{\text{ZFS}}^{zz} - \frac{1}{2}D_{\text{ZFS}}^{xx} - \frac{1}{2}D_{\text{ZFS}}^{yy}$, $E = \frac{1}{2}(D_{\text{ZFS}}^{xx} - D_{\text{ZFS}}^{yy})$. We assume a realistic value of $D = 25 \mu\text{eV}$ [63,64] and a low level of rhombicity, with $E/D = 0.02$. We suppose that the magnetic field is oriented along the z direction, i.e., $\mathbf{B} \equiv B\hat{z}$, with $B = 0.07$ T. Moreover, we consider a diagonal, isotropic $\mathbf{\Gamma}$ tensor, with components $\Gamma_{xx} = \Gamma_{yy} = \Gamma_{zz} = 2.0 \mu_B$, where μ_B is the Bohr’s magneton. After diagonalization of the Hamiltonian (39), the energy levels are labeled from 0 to 20 following an ascending order across the spectrum. Correspondingly, the associated eigenstates are labeled from $|0\rangle$ to $|20\rangle$. Since E is small, the anisotropy nearly represents a double-well potential. Eigenstates can then be associated with one of the two wells depending on the sign of $\langle S_z \rangle$. Note that the sign of D corresponds to an easy-plane anisotropy, with small values of $\langle S_z \rangle$ in low-lying states.

In order to show the link between the coherence factor of a superposition of two eigenstates and the relative Δ parameter as defined in Eq. (38) and depicted in Sec. IV B, we start by considering the set of seven lowest energy levels within the spectrum, $|0\rangle$ to $|6\rangle$. For each possible pair of states, a coherent superposition is prepared.

The characteristic values of Δ were calculated for each pair and are summarized in the legend in Fig. 1. They have been sorted in descending order. The associated color scale ranges from blue, representing the maximum value of Δ , to red, indicating the minimum. The coherence factor decays, computed by using the CCE method (up to second order), are displayed in Fig. 1. The timescale is normalized by taking as a reference the time employed by the fastest curve to reach the value of $1/e$, which is approximately $0.065 \mu\text{s}$. We also report in Fig. 1 a scatter plot of the time T_{decay} required for each curve to reach

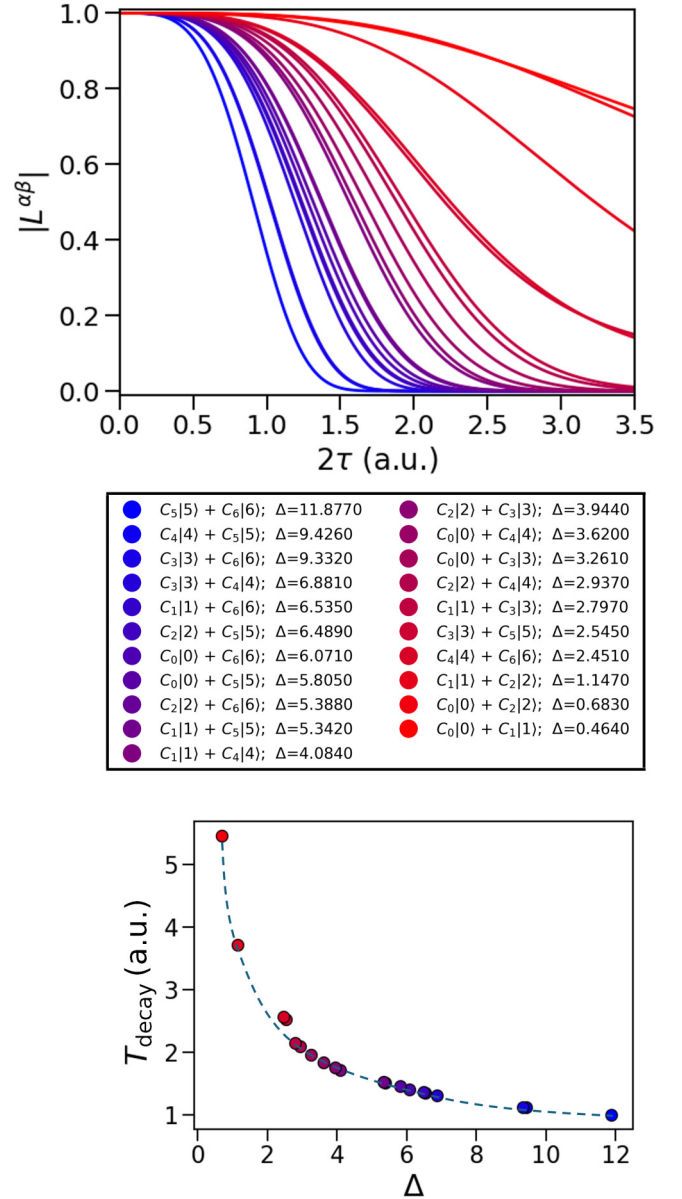


FIG. 1. Top: coherence factor over time for the pairwise superpositions of states corresponding to the seven lowest energy levels of the spectrum. Middle: legend displaying the representative color for each superposition and the corresponding value of Δ . The values of Δ have been sorted in descending order, with the color scale ranging from blue (maximum value of the parameter), to red (indicating the minimum). Bottom: T_{decay} (the time required for each curve to reach the value of $1/e$) as a function of the Δ parameter.

the value of $1/e$ as a function of the corresponding value of Δ . It is evident that, by gradually decreasing the value of Δ with a proper choice of α and β (going from blue to red through the color scale), it is possible to extend the decay time of the system coherence factor. This result is in perfect agreement with the theoretical calculations carried out in Secs. IV A and IV B, where we have shown that the lower the differences in the expectation values of the local spin operators on the two eigenstates of the superposition (and, therefore, Δ), the nearer we are to the ideal condition expressed by Eq. (23). We stress the fact that even differences on the second decimal digit of

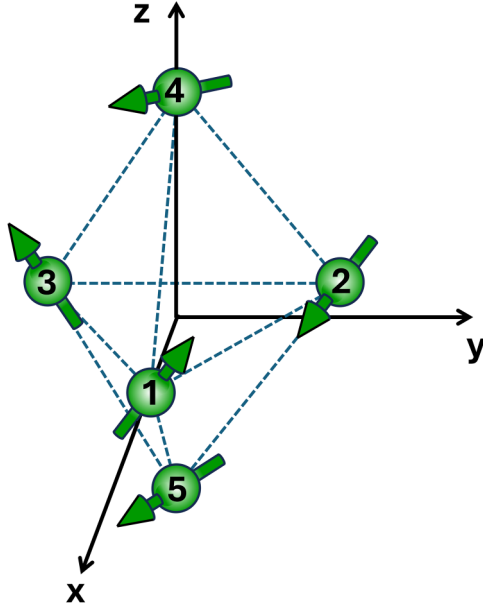


FIG. 2. Schematic structure of the system made of five spins 1/2. Spins 1–3 are placed at the vertices of an equilateral triangle lying on the x – y plane, while spins 4 and 5 are placed along the z axis. Each spin is positioned at a distance of 3 Å from the center. However, even when this symmetry is disrupted, the qualitative results remain unchanged. The resulting solid consists of a double tetrahedron.

Δ contribute to the ordering of the curves. It is important to notice that, in principle, one should evaluate the expectation values of the x and y components of S too, according to what has been stated in Eq. (35). However, in this specific case, those quantities are null $\forall \alpha, \beta$.

What we have shown so far is an illustrative example of the concrete implications of the theory developed in Sec. II. The more similar the eigenstates of a superposition from a magnetic point of view (expectation values of spin magnetic moments), the lower the value of Δ and, therefore, the longer the coherence time. Further insights can be gained by considering composite systems made of multiple spins spatially located in different positions, as it will be discussed in the following section.

B. System with competing interactions

According to the definition of the parameter Δ in Eqs. (37) and (38), we expect that the leading terms causing decoherence are differences in the expectation values of *local* spin operators, instead of *total* spin operators, as one could expect at first glance. To demonstrate this result, we propose as a second example a system composed of five $S = 1/2$ spins interacting through competing interactions, shown in Fig. 2.

The corresponding Hamiltonian is

$$H_S = \sum_{i,j} \mathbf{S}_i \cdot \mathbf{D}^{ij} \cdot \mathbf{S}_j + \sum_i \mathbf{B} \cdot \mathbf{\Gamma}^i \cdot \mathbf{S}_i, \quad (40)$$

where

$$\mathbf{D}^{ij} = \begin{pmatrix} J_x^{ij} & K_z^{ij} & 0 \\ -K_z^{ij} & J_y^{ij} & 0 \\ 0 & 0 & J_z^{ij} \end{pmatrix}$$

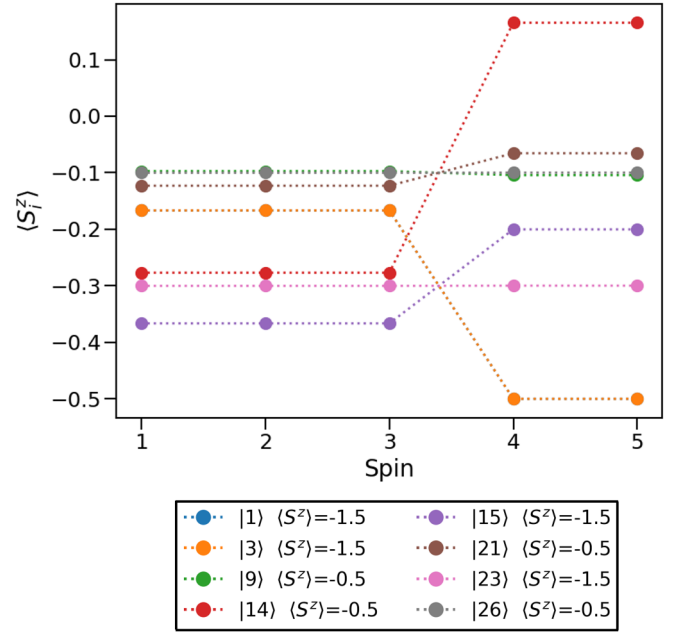


FIG. 3. Expectation values of the S_z^i operators for the eigenstates of the system considered in Sec. VB. In the legend, we reported the label of the states and the value of $\langle S^z \rangle = \sum_i \langle S_z^i \rangle$.

is the tensor describing the interaction between the spins i and j . For the antiferromagnetic interactions, we set $J_x^{ij} = J_y^{ij} = J_z^{ij}$, with $J_x^{12} = J_x^{23} = J_x^{31} = 0.3$ meV and $J_x^{1m} = J_x^{2m} = J_x^{3m} = 0.1$ meV, where $m = 4, 5$. $K_z^{ij} = J_z^{ij}/10$ are the components along the z axis of Dzyaloshinskii-Moriya interactions (DMIs). For this system, we choose $B = 1.0$ T and identical, diagonal, isotropic $\mathbf{\Gamma}^i$ tensors, with components $\Gamma_{xx} = \Gamma_{yy} = \Gamma_{zz} = 2.2 \mu_B$, as in Sec. VA. To illustrate the results, among the 32 energy levels, we selected the ones labeled as $|1\rangle, |3\rangle, |9\rangle, |14\rangle, |21\rangle, |26\rangle$ because they allow us to create a wide set of superpositions with different values of Δ parameter.

In Fig. 3, we report the expectation values of the S_z^i operators for the states considered above; only the z component is shown because the other ones are almost zero. Note that $\langle 1|S_z^i|1\rangle = \langle 3|S_z^i|3\rangle \forall i = 1, \dots, 5$, while the curves associated with the states $|9\rangle$ and $|26\rangle$ are very similar but not identical.

In Fig. 4, we report the coherence factor as a function of time, the arbitrary unit is the time required for the superposition $|\psi\rangle_{9,15}$ to reach the value of $1/e$ of the coherence factor (approximately $22 \mu s$). For each state $|\psi\rangle_{\alpha,\beta}$, we report the corresponding value of Δ parameter. Note that, for the state $|\psi\rangle_{1,3}$, the curve fluctuates around the maximal value because $\Delta = 0$; thus, the term $\tilde{R}$ in Eq. (31) cannot be neglected, as discussed in detail in Appendix B. Anyway, as outlined at the end of Appendix A, this is the ideal condition that we would like to achieve.

Moreover, the results show that, for each superposition, the difference in *total* spin $\langle \beta|S^z|\beta\rangle - \langle \alpha|S^z|\alpha\rangle$ does not explain the obtained coherence factor times. Consider, for example, the eigenstates $|9\rangle, |21\rangle, |26\rangle$. They have the same expectation value for the operator S^z , as seen in the legend of Fig. 3. Still, $|\psi\rangle_{9,26}$ shows a completely different coherence factor time

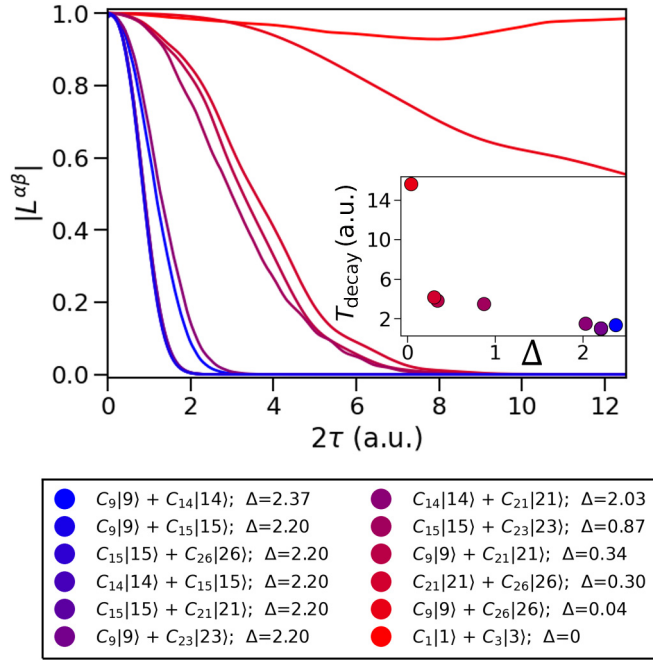


FIG. 4. Coherence factor curves for the superposition of eigenstates illustrated in the legend. The value of the Δ parameter is also shown. The arbitrary unit is the time required for the superposition $|\psi\rangle_{9,14}$ to reach the value of $1/e$ of the coherence factor. Inset: T_{decay} (the time required for each curve to reach the value of $1/e$) as a function of the Δ parameter.

compared to the states $|\psi\rangle_{9,21}$ and $|\psi\rangle_{21,26}$, thus this set of eigenstates cannot be considered to design a three-level qudit. These results can be completely explained only by comparing the expectation values of the local spin operators for the states $|\alpha\rangle$ and $|\beta\rangle$, involved in each superposition $|\psi\rangle_{\alpha,\beta}$. For this purpose, the Δ parameter estimates how far we are from the ideal condition where the coherence factor does not decrease.

Finally, note that the curves in Fig. 4 are not all ordered according to the corresponding Δ . This result does not contrast with the theory developed above. Indeed, the Δ parameter defined in Eq. (38) serves as a general measure associated with each pair of eigenstates and does not capture fine details. For example, the curve corresponding to the state $|\psi\rangle_{9,14}$, with $\Delta = 2.37$, decays slightly more slowly than the ones associated $\Delta = 2.2$. If the system contains more than one spin, this measure is no longer a fine descriptor of the rate of decoherence, as happened for the one-spin system described in Sec. V A, and the curves do not strictly follow the order established by the parameter. Anyway, it statistically well describes the observed coherence factor decay, confirming that the smaller the value of Δ , the longer the coherence time, in agreement with the theoretical results of Sec. II.

C. Qudit proposal

Equipped with the concepts learned through the examples in Secs. V A and V B, we started looking for a potential qudit candidate. Note that, to realize a *qubit*, it is enough to find two eigenstates of a system that maximize the coherence factor time of the superposition. Instead, for a *d*-level *qudit*, there

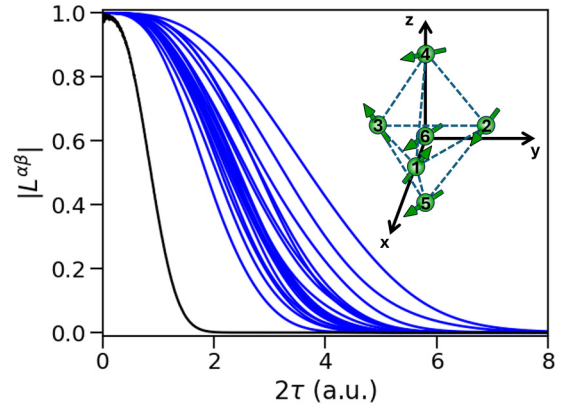


FIG. 5. The 21 coherence factor curves for the seven eigenstates with $S^z \approx 0$ of the AFM system (in blue). The uncoupled-spin curve, in black, is used to define the time scale arbitrary unit. Inset: The qudit proposal, obtained by adding a sixth $S = 1/2$ spin to the center of the triangular basis of the system with competing interactions depicted in Sec. V B.

are $d(d-1)/2$ pairs of eigenstates, each one prepared in a superposition with a specific coherence factor time. It follows that a qudit can be designed only if all the coherence factor curves are significantly longer than the gate operation time. As already demonstrated in the cases of the single giant spin and of the five-spin system with competing interactions, long coherence factor times can be obtained by choosing eigenstates with the appropriate expectation value of the local spin operators.

It must be emphasized that the search for a real molecular qudit candidate with the appropriate eigenstate structure is constrained not only by the requirement of minimal decoherence, but also by the practical limitations of implementation and manipulation. For these reasons, we carefully selected eigenstates with the following features: The perturbative Schrieffer-Wolff transformation described in Sec. II A must be valid, implying that the corresponding eigenvalues must not be nearly degenerate this condition was found to be satisfied for energy gaps bigger than 4×10^{-3} meV. Moreover, these eigenvalues should fall within a range of ≈ 0.4 meV that can be experimentally addressed by electromagnetic pulses in the microwave spectrum (X , Q bands) to ensure full connectivity between states; the magnetic matrix elements for transitions between them should be sufficiently large to enable qudit manipulation within a timescale of 10–100 ns, assuming pulses with an amplitude of the oscillating magnetic field of approximately 50 ns; and, finally, the selected states should not lie further than 1 meV from the ground state to minimize relaxation due to the emission of low-energy phonons.

To increase the number of states satisfying the constraints described above, we propose a system composed of six $S = 1/2$ spins (see Fig. 5, inset), obtained by adding a spin to the center of the triangular basis of the structure illustrated in Fig. 2. The corresponding Hamiltonian is shown in Eq. (40). Optimal qudits are obtained when the Zeeman term and the AFM exchange couplings are set to comparable values ranging from 0.1 to 1 meV, with the DMI approximately one-tenth

of these values. For instance, a possible choice is to apply a magnetic field slightly tilted away from the z axis to enhance the connectivity between eigenstates. Specifically, we set $B = 1.0$ T, tilted by $\pi/18$ rad around the y axis. Moreover, we supposed values of the exchange parameters to vary approximately from 0.5 to 0.1 meV, as detailed in Appendix C. Highly symmetric molecular structures are usually imperfect and often exhibit distortions. To avoid results that depend strictly on perfect symmetry, we introduce slight variations in the parameters to break it. The same random variation is applied to the gyromagnetic ratio tensors.

To single out the contributions of the eigenstate structure to decoherence, all the simulations have been performed considering the same bath used for the system described in Sec. V B. In order to highlight the effect of interactions, we have considered an isostructural system with uncoupled spins, thus setting the D^{ij} tensor in Eq. (2) equal to zero $\forall i, j$. The corresponding temporal decay is shown as a black curve in Fig. 5. The time instant at which the coherence factor reaches the value of $1/e$ is taken as a reference to set the timescale, which is approximately 15 μ s.

We selected seven eigenstates with $S^z \approx 0$, more details on the expectation values of the spin operators are given in the Supplemental Material [60]. We calculated the coherence factor decay for each of the corresponding 21 pair superpositions and reported the results with blue curves in Fig. 5. Since the Δ parameter is similar among these superpositions, the corresponding curves exhibit comparable decay behavior. Note that the coherence factor curves for all 21 superpositions show longer coherence factor times with respect to the reference noninteracting system. Moreover, the molecule exhibits full connectivity among all the levels, as the transition dipole moment for each pair of states is sufficiently large to enable transitions within a limited time. This nontrivial feature is highly advantageous for fully harnessing the potential of qudits, and is essential for implementing certain quantum algorithms. For instance, some quantum error correction algorithms designed for qudits require an all-to-all connection among levels [25,65]. We stress that there is room for further improvement in the optimization of the molecular spin qudit presented. Indeed, coherence times could be significantly extended through the optimization of the Hamiltonian parameters, like the magnitude of the exchange interactions, the amplitude and direction of the external magnetic field, and the appropriate selection of the states. Moreover, we proposed here a system made of spins $1/2$ only. An additional strategy would be the use of spins $S > 1/2$, increasing the number of degrees of freedom and, therefore, expanding the possible choice of eigenstates. However, this system can be seen as a prototypical example that embodies all the ingredients for the theoretical design of molecular spin qudits.

VI. CONCLUSIONS

In this work, we addressed the problem of decoherence in molecular spin systems at low temperatures. In particular, we focused on the pure dephasing resulting from the interaction of the central system with the surrounding nuclear spin bath. To do so, we developed a microscopic model of decoherence and implemented the CCE method to simulate the coherence

decay over time numerically. This approach allowed us to demonstrate a key result: The coherence of a superposition of two eigenstates $|\alpha\rangle$ and $|\beta\rangle$ is preserved if and only if the two Hamiltonian operators that describe the associated conditional bath dynamics commute with each other. For molecular spin systems, this condition translates into requiring identical expectation values of local spin operators for the two eigenstates. These eigenstates would generate a decoherence-free subspace if the second-order terms in the effective Hamiltonian were neglected.

While this ideal condition is rarely met in real systems, we introduced a parameter Δ to quantify the deviations, and we explored its impact on coherence times. Through numerical simulations, we validated our theoretical framework and demonstrated its applicability to systems ranging from single giant spins to composite structures with competing interactions. These insights allowed us to define a recipe for the theoretical design of molecular spin qudits. As a paradigmatic example, we proposed a composite system made of six spins $1/2$, interacting with each other through antiferromagnetic exchange interactions. We showed that it is possible to exploit competing interactions to create a viable qudit candidate, with many low-energy states characterized by full connectivity. This is highly beneficial for implementing quantum error correction schemes and other quantum algorithms, making such systems highly promising for quantum technologies. While the proposed qudit system represents a significant step forward, it is important to note that it does not yet constitute the optimal molecular spin qudit. In principle, further optimization of Hamiltonian parameters and state selection could extend coherence times and improve qudit performance. However, this system serves as a prototypical example to demonstrate how chemical tunability of spin interactions can mitigate decoherence, offering an interesting perspective for more robust quantum information processing platforms. The strategy developed here can be exploited in synergy with the mature approaches based on engineering the bath to push beyond the current limitations of spin qudits.

In conclusion, this work advances our understanding of decoherence in molecular spin systems and provides a practical framework for designing and optimizing molecular spin qudits, bringing them closer to practical implementations in quantum information processing.

ACKNOWLEDGMENT

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DATA AVAILABILITY

The data that support the findings of this article are openly available [66].

APPENDIX A: NEGLECTING THE SECOND-ORDER PERTURBED TERMS

Here, we will show how and why we can neglect all the commutators involving the H_{SB2} terms in Eq. (28) by

evaluating all the possible interactions acting on a generic spin belonging to the bath. Without loss of generality, we suppose a magnetic field acting along the z axis. Consider the last two terms in the Hamiltonian of Eq. (8). We can estimate these interactions, related to a bath spin located at position $\mathbf{r}$, as follows:

$$\begin{aligned} H_{SB1}(\mathbf{r}) &\approx m^z A(\mathbf{r}), \\ H_{SB2}(\mathbf{r}) &\approx 2 \frac{(m^z)^2}{\Delta E} A(\mathbf{r}) \sum_{\mathbf{d}} A(\mathbf{d}), \end{aligned} \quad (\text{A1})$$

where A is the mean interaction due to spin in position $\mathbf{d}$, ΔE is a typical energy difference between two system eigenstates, and m^z is the eigenvalue of the operator S^z relative to $|\psi\rangle$, i.e., the eigenstate we are taking into account. Considering Eq. (6), we infer that

$$A(\mathbf{r}) = \frac{\mu_0}{4\pi|\mathbf{r}|^3} \Gamma \gamma \quad (\text{A2})$$

and, by assuming a continuous and uniform distribution of spins into a sphere centered around the system, we find the following ratio:

$$\frac{H_{SB2}(\mathbf{r})}{H_{SB1}(\mathbf{r})} \approx \frac{m^z \mu_0 \Gamma \gamma}{2\Delta E} \left(\frac{1}{R_{\min}^2} - \frac{1}{R_{\max}^2} \right), \quad (\text{A3})$$

where $R_{\min}$ and $R_{\max}$ are, respectively, the minimal and the maximal radius for the sphere. The maximum value of this function ($R_{\max} = \infty$) is

$$\frac{H_{SB2}(\mathbf{r})}{H_{SB1}(\mathbf{r})} \approx 10^{-2}, \quad (\text{A4})$$

where we assumed $R_{\min} = 3 \text{ \AA}$ and typical values for ΔE , m^z , γ , and Γ . Thus, $H_{SB2}(\mathbf{r})$ is negligible with respect to $H_{SB1}(\mathbf{r})$ for each bath spin, regardless their position. It follows that the last commutator in Eq. (28) can be neglected with respect to the fourth and the fifth, which can be neglected with respect to the first one. Finally, the third commutator is smaller than the second one, leading to Eq. (33).

If the terms $(\langle \beta | S_k^\mu | \beta \rangle - \langle \alpha | S_k^\mu | \alpha \rangle) \Gamma_{\eta\mu}^k$ in Eq. (31) are small and comparable to $\tilde{R}$, Eq. (33) is no longer valid, and we can approximate Eq. (28) as follows. For each pair of spins (i, j) belonging to the bath with components (μ, ν) , we can compare the strength of the interactions due to $\mathbf{J}$ and $\mathbf{T}$ terms [see Eqs. (4) and (10), respectively]. We define the tensor Λ as

$$\Lambda_{\mu\nu}^{ij} = \left| \frac{T_{\mu\nu}^{ij}}{J_{\mu\nu}^{ij}} \right|. \quad (\text{A5})$$

Furthermore, we associate the following weight $\mathbf{P}$ to each coordinate:

$$P_{ij}^{\mu\nu} = \frac{|J_{\mu\nu}^{ij}|}{\sum_{i,j,\mu,\nu} |J_{\mu\nu}^{ij}|} \quad (\text{A6})$$

that is normalized by definition and becomes greater and greater as the interaction $J_{\mu\nu}^{ij}$ increases. The mean value of Λ can be evaluated as

$$\langle \Lambda \rangle = \sum_{i,j,\mu,\nu} \Lambda_{\mu\nu}^{ij} P_{ij}^{\mu\nu} = \frac{\sum_{i,j,\mu,\nu} |T_{\mu\nu}^{ij}|}{\sum_{i,j,\mu,\nu} |J_{\mu\nu}^{ij}|} \quad (\text{A7})$$

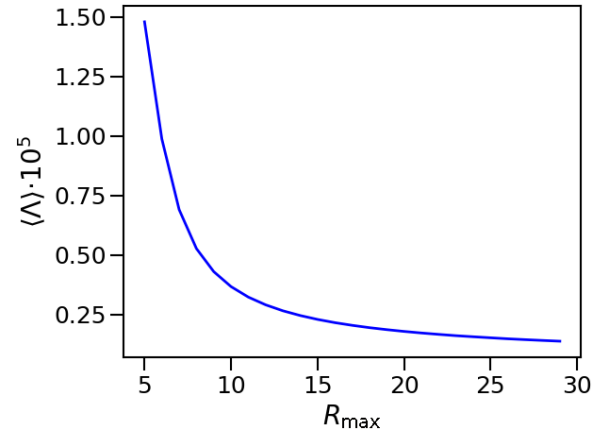


FIG. 6. Expectation value of Λ when the parameters assume the typical values encountered in MNMs.

that is equivalent to calculating the ratio between the sum of the absolute value of the interactions. We can estimate this mean value for typical systems by assuming a continuous distribution of spins into a sphere of radius $R_{\max}$ and obtain

$$\langle \Lambda \rangle = \frac{\mu_0 (\Gamma m^z)^2}{8\Delta E} \frac{(R_{\max}^2 - R_{\min}^2)}{R_{\max}^4 R_{\min}^4} \frac{1}{I}, \quad (\text{A8})$$

with

$$\begin{aligned} I &= \int_{R_{\min}}^{R_{\max}} \int_{R_{\min}}^{R_{\max}} \int_{t(r_1, r_2, l)}^{\pi} \frac{dr_1 dr_2 d\theta}{(r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta)^{3/2}}, \\ t(r_1, r_2, l) &= \arccos \left(\frac{r_1^2 + r_2^2 - l^2}{2r_1 r_2} \right), \end{aligned} \quad (\text{A9})$$

where l is the minimum distance between the bath's spins. By keeping l and $R_{\min}$ fixed, we see that the value of $\langle \Lambda \rangle$ decreases, while $R_{\max}$ increases as expected by considering the interactions involved in Eq. (A7). This consideration appears evident in Fig. 6, where we assumed $R_{\min} = 3 \text{ \AA}$, $l = 3 \text{ \AA}$ and typical values for the other parameters. Moreover, it can be noticed that the values of $\langle \Lambda \rangle$ are $O(10^{-5})$, allowing us to neglect the fourth and fifth term with respect to the second one in Eq. (28), as well as the sixth one with respect to the third. In this case, Eq. (28) reduces to the following:

$$\begin{aligned} [H^\alpha, H^\beta] &\approx \sum_{k,\mu,\eta} (\langle \beta | S_k^\mu | \beta \rangle - \langle \alpha | S_k^\mu | \alpha \rangle) \Gamma_{\eta\mu}^k O_\eta^k \\ &\quad + [H_B, \Delta H_{SB2}]. \end{aligned} \quad (\text{A10})$$

In this case, despite the fact that the differences $(\langle \beta | S_k^\mu | \beta \rangle - \langle \alpha | S_k^\mu | \alpha \rangle) \Gamma_{\eta\mu}^k$ no longer represent the key quantities linking the coherence factor to the structure of the system's eigenstates, we have still achieved the ideal condition corresponding to long coherence times. Indeed, even when it is the leading term in Eq. (A10), the second-order contribution ΔH_{SB2} is small by definition and, as a consequence, $[H^\alpha, H^\beta] \approx 0$, having a small impact on coherence times.

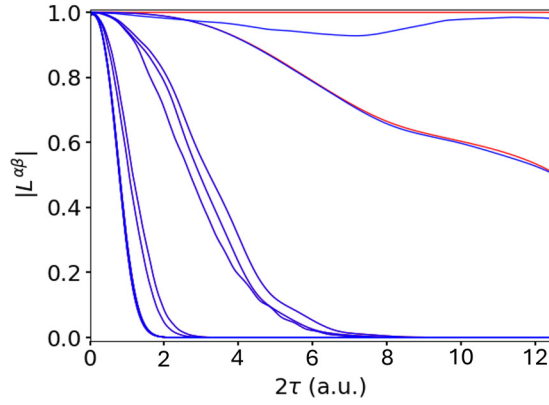


FIG. 7. For the system described in Sec. VB, we report the curves associated with a set of eigenstates: in blue, the one showed in Fig. 4; in red these eigenstates are computed by removing the terms (10) from the Hamiltonian.

APPENDIX B: NUMERICAL RESULTS AND SECOND-ORDER PERTURBED TERMS

Here, we investigate the contribution of the $\tilde{R}$ term to the coherence factor curves obtained for the system described in Sec. VB. In Fig. 7, we report in blue the curves shown in Fig. 4 and, in red, the ones obtained by removing the terms defined in Eq. (10) from the Hamiltonian [Eq. (8)]. In the latter

case, the term $\tilde{R}$ in Eq. (31) is zero and relation (33) is exact. We note that, for each pair of eigenstates, the faster they decay, the smaller the difference between the red and the blue curves: they are indistinguishable for each superposition except for the two with longer coherence times. By considering the discussion made in Appendix A, this is exactly what we expect: the more the differences between the expectation values of the spin operator become small (Δ parameter decrease), the more the coherence times become longer and the second order terms non-negligible because comparable with the leading terms.

APPENDIX C: PARAMETERS FOR THE HAMILTONIAN OF QUDIT PROPOSAL

Here, we report the values of all the parameters for the system described in Sec. VC. For the interaction between the spins we have

$$J_x^{ij} = J_y^{ij} = J_z^{ij}, \quad J_x^{12} = 0.5 \text{ meV}, \quad J_x^{23} = 1.01 J_x^{12}, \quad J_x^{31} = 1.08 J_x^{12}, \quad J_x^{14} = 0.1 \text{ meV}, \quad J_x^{24} = 0.95 J_x^{14}, \quad J_x^{34} = 1.03 J_x^{14}, \quad J_x^{15} = 1.10 J_x^{14}, \quad J_x^{25} = 0.89 J_x^{14}, \quad J_x^{35} = 0.98 J_x^{14}, \quad J_x^{45} = 0.1 J_x^{12}, \quad J_x^{16} = 1.1 J_x^{12}, \quad J_x^{26} = 1.05 J_x^{16}, \quad J_x^{36} = 0.93 J_x^{16}, \quad J_x^{46} = 1.05 J_x^{14}, \quad J_x^{56} = 0.92 J_x^{46}, \quad \text{and } K_z^{ij} = J_z^{ij}/10.$$

As stated in the main text, $B = 1 \text{ T}$ and tilted by $\pi/18$ rad around the y axis. We consider the following diagonal and isotropic gyromagnetic ratio tensors: $\Gamma_{xx}^1 = 2.210 \mu_B$, $\Gamma_{xx}^2 = 2.200 \mu_B$, $\Gamma_{xx}^3 = 2.180 \mu_B$, $\Gamma_{xx}^4 = 2.190 \mu_B$, $\Gamma_{xx}^5 = 2.205 \mu_B$, and $\Gamma_{xx}^6 = 2.195 \mu_B$.

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