I. INTRODUCTION

Recently, the physics of ring-shaped molecular magnets with antiferromagnetic interactions and an odd number of interacting spin centers (e.g., paramagnetic ions) has attracted a great deal of interest since they provide emblematic examples of systems where spin frustration effects due to quantum magnetism play a major role. Moreover, they have been synthesized and studied experimentally [1, 2, 3, 4, 5]. Specifically, we shall concentrate on the anomalous magnetic properties in some heterometallic odd spin rings [6, 7, 8, 9] namely, chromium rings. The system comprises eight chromium(III) ions with spin $S = \frac{3}{2}$ each, and one nickel(II) ion with spin $S = 1$. The magnetic properties of this first odd-member antiferromagnetic ring have been investigated with electron paramagnetic resonance (EPR) and its spin frustrated properties has been visualized by means of a M"obius strip. In this paper we propose an alternative and complementary picture of the ground state of this Cr8Ni ring molecule using valence bond states (VBS) [10, 11, 12, 13, 14, 15, 16, 17, 18] of virtual spins which are used to represent the spins $S = \frac{3}{2}, 1$ of the real constituent ions. We will show that the particular bond pattern acquired by these VBS states is a consequence and manifestation of the spin frustration in the odd Cr8Ni ring molecule.

Molecular nanomagnets are fascinating new magnetic materials [19, 20, 21]. They appear in a large variety of compounds with many different properties. We shall focus on antiferromagnetic compounds of bimetallic rings. These molecules are ideal candidates to study the physics of simple but nontrivial spin models like the AF Heisenberg interaction. The key point here is that, these molecules show very interesting finite-size quantum many-body effects which are typically overlooked in other studies of the Heisenberg model where the main focus is to achieve the thermodynamic limit (number of spins going to infinity). In those studies, the small finite-size effects are considered spurious effects that vanish for larger and larger systems, which eventually may show some sort of universality, if that is the case. Quite on the contrary, the nice thing of these small molecules is that we can vary its size and coupling constant strengths such that the finite-size effects become some real property that can be addressed experimentally, theoretically and numerically. Some interesting examples of these small quantum effects addressed experimentally, theoretically and numerically.

II. HAMILTONIAN DESCRIPTION OF THE CR8NI MOLECULE RING

Magnetic molecules are emblematic instances of an ensemble of non-interacting quantum systems embedded in a condensed matter environment. The synthesis of molecular magnets has undergone rapid progress in recent years. Each of those quantum systems are identical molecular units that can contain as few as two and up to several dozens of paramagnetic ions (spins). In
our case, they correspond to Cr8Ni ring molecules. This molecule is one of the many relevant molecules containing transition-metal ions whose spins are so strongly-exchange coupled that when the temperature is low enough, their behaviour is like single-domain particles with a certain total spin [19, 20, 21].

Macroscopically, these materials appear as crystals or powders. Nonetheless, their intermolecular magnetic interactions are utterly negligible when compared to their intramolecular interactions. Thus, measurements of their magnetic properties reflect mainly ensemble properties of single molecules. There are two major advantages in the research on these molecule aggregates. Firstly, the outstanding degree of accuracy by which their magnetic dynamics can usually be modeled. Secondly, the opportunity to chemically engineer molecules possessing desired physical properties [19, 20, 21]. In our case, the interest relies on the study of the Heisenberg model in situations that are usually discarded when studying that model in infinite one-, two-, and three-dimensional systems. Our studies will reinforce the idea that such spin arrays yield qualitatively new physics caused by the finite size of the system.

The Cr8Ni compound belongs to a wider family of molecular rings. In molecules with a small number of ions, there exist big differences in their physics depending on each particular compound. A first major difference is related to the number of its ions: odd or even. In this regard, the implications are mainly twofold: first, having a difference of one ion in the same family of molecules, can cause the molecule to have a neat magnetic moment or not, therefore changing its magnetic properties drastically. Second, and interestingly enough, a molecular ring with completely antiferromagnetic interactions between nearest neighbors ions can be a candidate to present quantum spin frustration properties if the number of atoms is odd, while this effect will not generally be present for even member rings in a given family compound.

As it happens, in the majority of these molecules the localized single-particle magnetic moments of the ions couple antiferromagnetically. Then, their spectrum is described rather well by the Heisenberg model with very few parameters because of the high symmetry of the molecular configurations. These coupling parameters correspond to isotropic nearest neighbor interaction sometimes augmented by anisotropy terms.

The Cr8Ni compound is one of the first antiferromagnetic odd member rings which has been artificially synthesized. The results of its magnetic properties are interpreted within the framework of a spin Hamiltonian approach and they nicely fit the pattern of the energy levels obtained by inelastic neutron spectroscopy. There exists also reports on its magnetic and spin frustration effects [1]. In view of these properties, it has been proposed [1] that the behavior of this molecule can be properly explained with a nearest neighbors Heisenberg model where only two different microscopic couplings play a role: one is the coupling that parametrized the strength of the interaction existing between the Ni ions and the neighbor pair of Cr. The other one is the coupling that takes into account the interaction between the Cr-Cr pairs, which can be considered the same for each pair. The easy-axis anisotropy term is reported to be very weak how as to play any role. Therefore, the Hamiltonian that we shall study has the following form:

\[ H = \sum_{i=1}^{7} S_{\text{Cr}}(i) \cdot S_{\text{Cr}}(i+1) + J' [S_{\text{Ni}} \cdot S_{\text{Cr}}(1) + S_{\text{Ni}} \cdot S_{\text{Cr}}(8)], \]  

where, for convenience, the Cr atoms have been numbered from 1 to 8, being these latter the two neighbors of the Ni atom. Notice that, since the spin of the nickel is equal to \( S_{\text{Ni}} = 1 \) and the spin of the Cr atoms is \( S_{\text{Cr}} = 3/2 \), the total spin of the molecule must be integer.

In fig. 1 we have plotted some lowest lying energy levels of this Hamiltonian. In Sect. IV we shall explain how these numerical results have been obtained with a multi-target Lanczos method. It can be observed that, in some regime of the coupling constants \( J' \) and \( J \), the energy levels are highly braided and, as a consequence, the ground state has different value of the total spin depending on the exact value of these couplings. However, as can be seen from the inset of this figure, for large values of \( J' \) the ground state is always a spin singlet with a triplet state very close in energy above it. In this work, we will restrict our study to the antiferromagnetic \( (J' > 0) \) region and in particular to the region where the ground state is a singlet and the first excited state is a triplet very close in energy.
state is a singlet. From fig. [1] we see that this area corresponds to \( J' > 1.5 \text{ K} \), while the region \( 0 < J' < 1.5 \text{K} \) is characterized by a ground state with total spin equal to one (for convenience the computations in fig. [1] have been done with a fixed value of \( J = 16 \text{ K} \)).

The interest in the domain where the ground state is a singlet comes not only from the fact that it spans the most extension in the antiferromagnetic area, but also because the physics of the real Cr8Ni seems to be in agreement with a regime close to \( J = 16 \text{ K} \) and \( J' = 70 \text{ K} \), with a non-magnetic ground state. Therefore, the interest of our study relies on the fact that it can provide new insights into the physics of a not so well-known state of matter but with a well defined connection with experiments in real compounds.

III. IMPURITY INDUCED VBS PICTURE

A valence bond solid is a particular quantum many-body state that can be understood as follows: given a system of real particles with total spin \( S \), we can split each one of them into \( 2S \) virtual particles of spin \( S = 1/2 \). In order to recover the original spins, we enforce these virtual particles to couple (i.e., symmetrize) among themselves in order to give the original spin \( S \) particles. To create now a wavefunction with total spin equal to zero, we make singlets (i.e., antisymmetrize) out of every pair of virtual particles.

We will denote each of these singlet pairs between virtual particles as a bond. There are a lot of different possible ways to fix the bonds between all the virtual particles and, in general, the total wave-function may have contributions from all these configurations. There exist however some physical situations in which only some particular bond configurations, out of the whole possible set, take part in the wave-function: some systems have a major contribution coming only from one particular bond arrangement. These systems are commonly dubbed bond crystals. It may also happen that there exist not one but some few bonds configurations whose weights are dominant in the total wave-function. In this case the system is called a resonating valence bond solid (RVBS). There exist yet another kind of more disordered states, denoted \((m,n)\)-VBS, which we shall see that describe properly the ground state of the Cr8Ni in the singlet region. A general \((m,n)\)-VBS state is built by forming bonds only between virtual spins belonging to neighbor real particles, with the numbers \( m, n \) satisfying \( m + n = 2S \) and \( S \) being the spin of the real particle.

These states are usually translationally invariant (with the \((m,n)\)-VBS notation this means that \( m = n \)) in those systems where the Hamiltonian possess this symmetry. There also exist dimerized \((m,n)\)-VBS states that have been shown to appear in systems where the full translational symmetry of the Hamiltonian has been partially broken such that still exist an enlarged unit cell. Typically, this effect can be obtained by introducing an external dimerization coupling constant in the Hamiltonian that still preserves some periodicity.

Our main result in this section is that there is another mechanism to provide such dimerized \((m,n)\)-VBS states in the Cr8Ni ring molecule and whose success precisely resides in the existence of an impurity within an homogeneous system. To understand this mechanism in the particular case of the Cr8Ni, we resort to the strong coupling limit where the antiferromagnetic interaction between the \( Ni \) and its neighbors is much larger that the interaction among \( Cr \) pairs. As shown in fig. [2] the two virtual spins comprising the \( Ni \) will be likely to form bonds with the virtual particles in the neighbor chromiums to satisfy their antiferromagnetic constraints. The rest of the virtual spins left will then tend to form similar bonds with their neighbor partners, giving as a result a dimerized non translationally invariant VBS. We would like to stress the fact that the validity of this picture is rooted in the existence of the \( Ni \) impurity. In fact, the physics of a homogeneous system of \( Cr \) atoms is closer to a gapless critical phase rather than to such a gapped state.

General \((m,n)\)-VBS states belong to a class of spin liquids which are known to possess an special hidden order that can be identified by a particular non-local order parameter called the string order parameter (SOP) \([22, 23, 24, 25, 26, 27]\). This order parameter has proved itself extremely successful in the task of characterizing diverse kinds of such states, both in the pure one dimensional cases and also in less trivial systems such as ladders \([25, 27]\). We shall see that this parameter also allows us to characterize the Cr8Ni ground state. The definition of the generalized string order parameter is as follows \([24]\):
\[ O_{\text{str}}(\theta) = \lim_{|j-i| \to \infty} (S_i^z \exp(i \theta \sum_{k=i}^{j-1} S_k^z) S_j^z). \] (2)

FIG. 3: Representation of two ways to measure the SOP in the Cr8Ni ring choosing adjacent starting sites. In the diagram at the top we break two bonds at the left end and one at the right. This corresponds to a (2,1)-VBS. In the diagram at the bottom we have the same physical configuration but now we are breaking one bond at the left and two at the right end, which characterizes a (1,2)-VBS. Notice that both measures have been taken with an odd number of sites, otherwise the SOP is zero.

The limit \(|j-i|\) going to infinite must be understood as comprising a region large enough so as to neglect finite-size effects. In our case the system itself is finite, however we will see that the results are still conclusive despite some corrections that have to be considered due to this fact.

We hereby summarize the most relevant properties of the SOP for our purposes:

i/ The SOP is symmetric with respect \(\theta = \pi\).

ii/ The imaginary part of the SOP vanishes as we consider larger systems.

iii/ Due to the fact that the definition of the SOP makes use of antisymmetric operators under spin flip, the number of sites considered in the measure must be odd in order to have an even number of these operators. Otherwise the SOP is zero.

iv/ Given a generic \((m,n)\)-VBS state, the number of zeros of this operator in the interval \(\theta \in [0,2\pi]\) coincides with the number \(m\).

v/ Two measures of the SOP beginning in adjacent sites will differ in the order of the numbers \(m\) and \(n\). That is, if one measure gives a \((m,n)\)-VBS state, the other will be a \((n,m)\)-VBS (see fig. 3).

In order to show the existence of a VBS-picture of the Cr8Ni molecule as described in fig. 2, we have computed the generalized string order parameter in the ground state of the molecule for different ratios of the coupling constants \(J\) and \(J’\). In virtue of property iv/ above we can characterize the VBS state counting the number of zeros of this operator. Moreover, we have some freedom at choosing the starting and end sites to measure the SOP (i.e., the numbers \(i\) and \(j\) in definition (2)) and we will see that the results are consistent with property v/.

In fig. 4 we have plotted the SOP computed in two different blocks of the ring and adjacent starting sites (these blocks are represented in fig. 3). Remarkably, even in this small molecule, the imaginary part of the SOP vanishes in all our computations.

In fig. 4a, the curves with high values of \(J’\) have two local minima in the interval \(\theta \in [0,2\pi]\) whose value is compatible with zero considering that the system is finite and the block used to measure the SOP comprises only some few spins. This result is consistent with a (2,1)-VBS. The shape of the SOP is also typical of these states, with two noticeable maxima placed approximately at \(\theta = \pi/4\) and \(\theta = 3\pi/4\). Accordingly, the computations shown in fig. 4b shall be consistent with a (1,2)-VBS as explained above. We see that again the shape of the SOP for the strong coupling curves shares the main features of these states, that is, one substantial maximum placed precisely at \(\theta = \pi/2\). There is however a major difference at \(\theta = 0\).
and \( \theta = \pi \), where the SOP does not vanish but has a significant negative value. At these points the exponentials in the definition of the SOP do not play any role and hence it is a usual spin-spin correlator between the two \( Cr \) atoms at the end of the block. Since our ring is finite and closed it is quite natural to think that the \( Cr_1 \) and \( Cr_7 \) spins are highly correlated via the spin frustration in the \( Ni \) impurity. Therefore, such as finite value at \( \theta = 0 \) only shows the compromise between the bulk (1, 2)-VBS picture of the whole system and the local physics of those spins.

In summary, the string order parameter reveals that the ground state of the \( Cr8Ni \) in the strong impurity coupling limit is consistent with a impurity-mediated mechanism of spin frustration, the result of which is the VBS-pattern shown in fig.2 Since we are dealing with a finite system the possibilities to drastically change the nature of the ground state are limited, that is, the possibility of a quantum phase transition is excluded and only a crossing with another energy level can produce this effect. Therefore, the intermediate \( J'/J \) regime can be considered as some deformation of the strong coupling limit. As we decrease \( J' \) and the \( S_{tot} = 1 \) state crosses the \( S_{tot} = 0 \), the VBS picture breaks down and the measures of the SOP are not meaningful in the sense that the properties of this operator in such a state are not well defined.

IV. FRUSTRATION AND DYNAMICS IN CR8NI

As we have already mentioned, the \( Cr8Ni \) ring molecule is frustrated in the sense that the minimum energy of the system can not be obtained minimizing separatedly each of the two body terms of the Hamiltonian (1). Another way to see it is by resorting to the classical limit where each spin is pictured as a classical vector. Once we set the value of one of those classical spins, then we can fix one by one the rest of the spins in order to minimize the local interactions, but in the end there will be one spin for which the local interaction with both of its neighbors can not be minimized at the same time.

Typically, systems where frustration exists come along with a rich and very often not so well-known physics. Roughly speaking, we can say that frustration in general increases the complexity of those systems, both in the physics they exhibit as well as in the way to approach them. In particular, there is not a well defined way to measure the amount and localization of frustration. An attempt to quantify these effects in \( Cr8Ni \) can be done attending to the structural changes of the ground state as we vary the couplings. That is, by inspection of the way in which spins in the ring couple to form the final state. This procedure has a connection with experimental techniques where the Lande factors of the ring can be measured. However this procedure is not suitable to study a rotationally invariant singlet ground state where the spin is zero. In this section we will study the behavior of the \( Cr8Ni \) molecule by means of computing the time evolution of some important spin correlators: the spin autocorrelation of the impurity \( Ni \) atom with itself and the spin correlation between the \( Ni \) atoms and each \( Cr \) along the ring. These correlators correspond to the vacuum expectation value of the time-evolved spin operators \( S_{Ni}(t) \) and \( S_{Cr_i}(t) \) projected onto the spin operator of the \( Ni \) impurity at \( t = 0 \), \( S_{Ni}(0) \). This is a way to dynamically probe the spin structure in the ground state \( |\psi_0\rangle \) of the ring molecule. In fact, we shall consider the square modulus of those correlators and interpret them as time-evolution probabilities. That is, we shall consider the following correlators in order to construct a figure of merit:

\[
C_{Ni}(t) := \langle \psi_0 | S_{Ni}(t) \cdot S_{Ni}(0) | \psi_0 \rangle, \tag{3}
\]

and

\[
C_{Cr_i}(t) := \langle \psi_0 | S_{Cr_i}(t) \cdot S_{Ni}(0) | \psi_0 \rangle, \tag{4}
\]

Notice that in a rotationally invariant singlet ground state \( |\psi_0\rangle \) the correlations in the \( x, y \) and \( z \) axis have the same value and thus, the expressions above can be written as:

\[
C_{Ni}(t) = 3 \langle \psi_0 | S_{Ni}^z(t) S_{Ni}^z(0) | \psi_0 \rangle, \tag{5}
\]

\[
C_{Cr_i}(t) = 3 \langle \psi_0 | S_{Cr_i}^z(t) S_{Ni}^z(0) | \psi_0 \rangle, \tag{6}
\]

Since the proportionality factor does not provide any additional information we will discard it from now on and will consider the bare \( z \)-axis projection correlators. The time dependency of the operators is given by the usual Heisenberg picture:

\[
O(t) = e^{iHt} O(0) e^{-iHt}. \tag{7}
\]

The idea behind this figure of merit to measure the dynamical correlations between spins is similar to the static correlator used to measure spin correlations in space separated sites \( i \) and \( j \) of the ring \( \langle \psi_0 | S_{Cr_i}(i) \cdot S_{Ni}(j) | \psi_0 \rangle \). This static correlator measure spatial correlations, while our purpose is to measure time-evolved correlations which will probe not only the ground state physics but also the excited states physics.

We next explain briefly the numerical method used to evaluate these correlators. After that we shall show and discuss the results.

A. Numerical Method

The Hamiltonian (1) is SU(2) rotational invariant. That is, it commutes both with the total spin and the \( z \)-axis projection of the total spin. In table I we show the dimensions of the subspaces corresponding to the conserved quantum numbers of these operators. These sizes are in the limit to perform exact diagonalization
but lie however within the domain reachable for a Lanczos method.

To do our computations we will make use of an adapted version of the Lanczos algorithm specific to compute real-time dynamics [33, 34, 35]. In this framework it can be shown that the correlators written above can be expressed as:

\[ C_i(t) = \sum_{j=0}^{M} \langle \psi_0 | S^{z}_{Cr}(t) | S^z_{Ni}(0) \rangle \langle \tilde{\psi}_j | S^z_{Ni}(0) | \psi_0 \rangle e^{-i(\tilde{\epsilon}_j - E_0)t}, \]

where \( M \) stands for the dimension of the Krylov space \( \mathcal{K}(H, q_0, M) \) such that \( \mathcal{K}(H, q_0, M) = \mathcal{K}(H, q_0, M + 1) \) with \( q_0 := S^z_{Ni} | \psi_0 \rangle \). That is, \( M \) is the dimension of the largest invariant subspace generated by successive applications of the Hamiltonian \( H \) upon the seed vector \( q_0 = S^z_{Ni} | \psi_0 \rangle \). The vectors \( | \tilde{\psi}_j \rangle \) are the approximated eigenvectors computed in this Krylov subspace, \( \tilde{\epsilon}_j \) are the energies of these eigenvectors and \( E_0 \) stands for the energy of the ground state.

The number \( M \) is typically much lower than the total dimension of the Hilbert space, but still high to numerically compute a complete basis of the Krylov subspace. Therefore, the approximation in this method resides in the fact that we will substitute the dimension \( M \) with a lower number of vectors that still serve as a complete basis for these correlators.

In order to obtain the most accurate results and representations of the eigenvectors of the Hamiltonian \( | \tilde{\psi}_j \rangle \) we have not used the same Krylov space to compute them all. Instead we have performed a Lanczos iteration to find the ground state. After that, the Lanczos iteration is restarted with the previously found eigenvectors projected out of the subspace to find the next excited state. And so on and so forth, until we have computed the desired number of eigenvectors. In particular, to compute the correlators described before we have used 400 eigenvectors of the Hamiltonian. As regards of the tolerance in the eigenvalues, we have set it to \( 10^{-14} \) allowing a maximum dimension of each Krylov space of 350 vectors. Were we in an exact situation, these vectors should be normalized to one and be orthogonal among themselves. Let us call \( V \) the matrix whose columns are these eigenvectors. We have checked that we obtain the following accuracy,

\[ ||V V^T - 1|| \sim 10^{-4}, \tag{9} \]

which can be considered a low value for such a large number of eigenvectors. Moreover, as another check of the accuracy of the eigenvectors we have computed the total spin of each one of them and we have obtained integral values up to precisions of \( 10^{-6} \) in the vast majority of them. As for the invariance of the Hamiltonian under reflection with respect the \( Ni \) atom, we have checked that symmetric one and two body correlators evaluated on every eigenvector are the same up to the fourth or fifth decimal digit.

\[
\begin{array}{|c|c|c|}
| J' \; | \; C_{Ni}(0) \; | \; \text{Error} \; | \\
|---|---|---|
| 2 \; | \; 0.66666 \; | \; 0.00002 \; |
| 10 \; | \; 0.66666 \; | \; 0.0000 \; |
| 20 \; | \; 0.6653 \; | \; 0.02 \; |
| 30 \; | \; 0.66512 \; | \; 0.2 \; |
| 40 \; | \; 0.65660 \; | \; 2 \; |
| 50 \; | \; 0.57469 \; | \; 14 \; |
\end{array}
\]

Table II: Relative error between the Ni self-correlation at \( t=0 \) using [33] with \( M=400 \) eigenstates and the value \( \langle \psi_0 | S^z_{Ni} S^z_{Ni} | \psi_0 \rangle \) in the ground state, which is equal to 2/3.

In order to check how complete is our set of eigenvectors, we have compared the value at \( t = 0 \) computed using [33] and [34] with the values obtained measuring the correlators in the ground state without the projectors in between. We have observed that the agreement is excellent for low values of \( J' \) while it goes worse for higher values of the coupling constant. Table II shows these values and the relative error.

These accuracy checks confirm that our numerical results are good enough so as to interpret them on physical grounds with respect to the spin frustracion effects described in previous sections.

\[ B. \; \text{Results} \]

In the previous sections we have proposed and checked with the proper order parameters a static picture of the ground state of the Cr8Ni ring. In the limit when the \( Ni \) is weakly coupled to the \( Cr \) bulk (\( J'/J \ll 1 \)) the system

| \( S_{tot},\pm S_{tot} \) | Dimension | Dimension |
|---|---|---|
| 0 | 1000 | 23548 |
| 1 | 2764 | 22548 |
| 2 | 3905 | 19784 |
| 3 | 4256 | 15879 |
| 4 | 3900 | 11623 |
| 5 | 3605 | 7723 |
| 6 | 2150 | 4628 |
| 7 | 1308 | 2478 |
| 8 | 692 | 1170 |
| 9 | 314 | 478 |
| 10 | 119 | 164 |
| 11 | 36 | 45 |
| 12 | 8 | 9 |
| 13 | 1 | 1 |
| Total: | 196608 | 196608 |

Table I: Dimension of each subspace with well defined quantum numbers out of the total Hilbert space of a Cr8Ni ring. The second column corresponds to the subspaces with well defined total spin. The third one are the sectors with well defined value of the z-axis projection of the total spin. In this last case for each value in the first column we must consider the positive and negative cases.
we have plotted the correlators (4) and (5, 6) is accurately described by an isolated Ni atom with itself and with the rest of the Cr atoms. The graphs have been done with a value $J = 16$ K and: a) $J' = 2$ K, b) $J' = 10$ K, c) $J' = 20$ K. For convention the sign of the correlators has been chosen to coincide with the sign of the correlation at $t=0$, which is a real number.

In figs. 5 and 6 we have plotted the correlators (5) and (4) for a fixed value of the constant $J = 16$ K and different values of $J'$. The Cr8Ni ring is invariant under reflection respect the impurity site and therefore we will only provide the correlators with the Ni itself and the Cr atoms numbered from 1 to 4 (with the notation of fig. 2), the correlations with the Cr atoms numbered from 5 to 8 are the same as their symmetric counterparts. We want to provide these magnitudes with the meaning of a time-evolved probability and hence we will consider only their modulus. It is worth noticing that the time correlators mentioned before, at $t = 0$ are real numbers whereas for arbitrary values of $t$ they are complex numbers. For convention, in the graphs where we plot the modulus of these correlators we will provide them with the same sign of their real value at $t = 0$ to make explicit the ferromagnetic or antiferromagnetic nature that they possess in the static $t = 0$ ground state.

In fact, we can observe in these graphs that the fingerprint of an antiferromagnetic order is present in the initial $t = 0$ ground state and shows up in the alternation
of the signs of the correlators. Notice also a signal of frustration in the fact that this alternation fails in the \( \text{Cr}_3 \) and its symmetric counterpart \( \text{Cr}_5 \) (due to the reflection invariance of the ring their value is equal with the same sign), where the correlations reveal that both spins are oriented in the same direction respect the spin of the \( \text{Ni} \). Remarkably this ferromagnetic defect is a consequence only of the reflection invariance of the Hamiltonian.

From these graphs we can also infer that the average correlation of each spin with the impurity is little sensitive to the strength of the coupling constant \( J' \), although the amplitude of the deviations with respect to this average value increases with it.

The most important observation is that the dynamics of the correlators exhibit a non trivial sort of periodicity. That is, from the shape of the curves it seems that there exists many modulating components but a dominant pattern of oscillations is apparent. Moreover, the frequency of this pattern clearly increases with increasing values of the impurity coupling \( J' \), i.e. as we move towards more frustrated regimes, but not in the same way for all the spins. We have captured in fig. 7 the frequency of the dominant oscillatory pattern of each correlation. The graph highlights two different tendencies of the correlations depending on the considered spins: the frequency of the \( \text{Ni} \) self correlation as well as the correlations of the \( \text{Ni} \) spin with the \( \text{Cr}_1 \) and \( \text{Cr}_2 \) spins increase with \( J' \). Moreover in the case of the \( \text{Ni} \) self correlation the relation of these two variables is linear up to a high precision. In the case of the \( \text{Cr}_3 \) and \( \text{Cr}_4 \) spins the frequency is hardly affected by \( J' \).

![Graph showing number of oscillations per time unit vs. \( J' \)](image)

**FIG. 7:** The number of oscillations has been obtained counting the number of minima in a wide time interval and dividing by the total time. The \( \text{Ni} \), \( \text{Cr}_1 \) and \( \text{Cr}_2 \) have increasing frequencies with \( J' \) which corresponds to more frustrated regimes. In particular for the \( \text{Ni} \) spin the relation of these variables is linear up to a high precision. In the case of the \( \text{Cr}_3 \) and \( \text{Cr}_4 \) spins the frequency is hardly affected by \( J' \).

In this case the ground state is not rotationally invariant and the \( z \)-axis projection of the correlators is not proportional to the scalar correlators (3) and (4). For our purposes however, these magnitudes suffice to realize the different nature of both the singlet and triplet ground states: first of all is that not one but two dominant patterns of oscillation are well distinguishable in the triplet regime. Secondly and also a major difference is that the scale in this regime is some orders of magnitude smaller than the singlet case.

The existence of this oscillatory behavior seems natural in a frustrated system where there does not exist a natural equilibrium position for each spin or where the resulting equilibrium configuration may result unstable. In a system composed by classical spins these oscillations can be interpreted as the necessary movements of each spin to satisfy the frustrated interactions, becoming faster as we blur the concrete equilibrium positions with the frustrating interactions.

The results in fig. 8 point towards a regime where the frustration introduced by the \( \text{Ni} \) impurity has strong local dynamical effects in the nearest and next nearest \( \text{Cr} \) neighbors while the rest of the spins perceive the impurity screened by this closer shell of atoms and therefore their dynamics is little affected by it. These results also show that the correlators proposed to study the frustration of the system indeed have the behavior expected for a suitable estimator in order to measure the intuitive idea we have about the amount of frustration in a certain system.

**FIG. 8:** Modulus of the spin correlation of the impurity \( \text{Ni} \) atom with itself and with the rest of the \( \text{Cr} \) atoms. The values of the coupling constants are \( J = 16 \) K and \( J' = 1 \) K which corresponds to the region where the ground state is a triplet. For convention the sign of the correlators has been chosen to coincide with the sign of the correlation at \( t = 0 \), which is a real number.

In recent years, considerable efforts have been devoted to synthesizing and investigating magnetic systems of nano scale dimension that comprise a controllable number of transition metal ions. Highly symmetrical clus-
ters of almost planar ring shape are among such topical molecular nanomagnets. In particular, the bimetallic ring molecule Cr8Ni is the first antiferromagnetic ring with an odd number of spins. Thus, it is a remarkable quantum system to test fundamental magnetic properties, and in particular the spin frustration effects.

In this work, we have studied the Cr8Ni frustrated ring in the regime where the ground state is a singlet. That is, with a fixed value $J = 16$ K this region corresponds to $J' > 1.5$ K. In this regard, the experimental characterization of a Cr8Ni molecule places the real strengths present in the real system close to $J = 16$ K and $J' = 70$ K, well within the singlet regime.

As we let the interaction strength of the Ni impurity to be stronger than that between the Cr atoms, the ring stabilizes in a ground state with the quantum properties of a dimerized VBS. The picture that explains this behavior in terms of the possible bonds between neighbor particles comes clear from fig. 2. Such a VBS state constitutes an example of a spin liquid with an intrinsic order that can be measured by means of some particular non-local order parameters. In fig. 4 we show the computations of this order parameter on the ground state and its behavior supports nearly the VBS picture. In this regard, some finite size effects can be observed in the order parameter that reveal a competition between the physics in the bulk of the ring and the strong effects, possibly mediated by the system frustration, that occurs in the vicinity of the Ni atom.

In the second section of this paper we have studied the role of the frustration in such a VBS state by means of computing the real time evolution of the spin correlators between the atoms in the ring. In particular, we have found that the amount of frustration can be related to the frequency in the oscillatory behavior of this correlators. This relation can be naturally established from the observation that the oscillations in the system become faster as we move to the more frustrated regime $J' \gg J$. Such an oscillatory behavior is natural in a system where no natural equilibrium is allowed due to the frustration. However, the spin correlators reveal that the atoms that are most affected by this frustration are the Ni impurity itself and those Cr atoms that are closer to it, that is Cr1 and Cr2, while the effect of the impurity strength seems to be less influent in the Cr3 and Cr4 atoms.

We believe that the methods and numerical techniques used in this work are versatile enough and can be extended to a variety of other nanomolecular magnetic compounds.

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