Spin frustration and fermionic entanglement in an exactly solved hybrid diamond chain with the localized Ising spins and mobile electrons

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The strongly correlated spin-electron system on a diamond chain containing localized Ising spins on its nodal lattice sites and mobile electrons on its interstitial sites is exactly solved in a magnetic field using the transfer-matrix method. We have investigated in detail all available ground states, the magnetization processes, the spin-spin correlation functions around an elementary plaquette, fermionic quantum concurrence and spin frustration. It is shown that the fermionic entanglement between mobile electrons hopping on interstitial sites and the kinetically-induced spin frustration are closely related yet independent phenomena. In the ground state, quantum entanglement only appears within a frustrated unsaturated paramagnetic phase, while thermal fluctuations can promote some degree of quantum entanglement above the non-frustrated ground states with saturated paramagnetic or classical ferrimagnetic spin arrangements.

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I. INTRODUCTION

The entanglement of physical states unveils the presence of non-local correlations in quantum spin systems that have no classical counterpart [1, 3]. Recently, the theoretical and experimental study of quantum entanglement has been put forward by a possibility of information processing at the quantum level [4]. The generation and manipulation of entangled states are fundamental in quantum information processes such as quantum computation [5], teleportation [6, 7], cloning of quantum states [8] and quantum cryptography [9]. Along this direction, condensed matter systems play a central role in the study of quantum entanglement, because several quantum devices have been proposed on the basis of solid-state systems. It has been demonstrated that quantum entanglement can affect the low-temperature behavior of macroscopic properties, such as the magnetic susceptibility and specific heat [10–13]. This fact has raised the interest in exploring the relation between quantum entanglement and thermodynamic macroscopic observables [14].

Within the above scenario, quantum spin chains serve as ideal model systems in studies of entanglement signatures [15, 17]. In particular, it has been shown that quantum entanglement exhibits a characteristic scaling behavior in a vicinity of the quantum critical point present in a class of one-dimensional quantum spin systems [15]. This feature has opened a new perspective for the description of quantum phase transitions [19–21] and resulted in the introduction of new quantities to measure the degree of quantum entanglement such as the quantum concurrence [22, 23].

The quantum Heisenberg spin chain is the prototype model used to search for entanglement signatures in the thermodynamic properties of magnetic systems [15, 24–28]. In an isotropic Heisenberg system composed of two qubits, the quantum concurrence decreases as a function of temperature until it completely vanishes at a characteristic threshold temperature, which depends on the applied external magnetic field. Further, the degree of quantum entanglement decreases monotonically with increasing the magnetic field for all temperatures [24]. On the other hand, Starace et. al. [27] showed that the anisotropy and external field can be used to produce and control in a two-qubit XY Heisenberg chain the degree of quantum entanglement at any finite temperature.

In the last two decades, quantum diamond spin chains have been also subject to extensive investigations. The spin-1/2 Heisenberg diamond chain [29–37] as well as its simplified Ising-Heisenberg version [38–41] have been largely explored in connection with a possible interplay between geometric spin frustration and quantum fluctuations. These systems display a rich variety of unusual physical properties such as magnetization plateaus [35, 36, 40], doubled peaks in the specific heat and susceptibility [33, 36] and quantum entanglement [37]. In addition, magnetic properties of A$_2$Cu$_3$(PO$_4$)$_4$ with A=Ca,Sr [42–44], Cu$_3$(TeO$_3$)$_2$Br$_2$ [44], K$_3$Cu$_3$AlO$_2$(SO$_4$)$_4$ [45], Cu$_3$(CO$_3$)$_2$(OH)$_2$ (azurite) [46] and Cu$_3$(OH)$_5$(NO$_3$) (likasite) [47] are satisfactorily captured by various versions of the spin-1/2 Heisenberg diamond chain. High-field magnetization measurements on the natural minerals azurite and likasite have for instance confirmed an existence of one-third [46] and two-thirds [47] magnetization plateau besides the double peaks in the relevant thermodynamic response functions.

A presence of the intermediate magnetization plateau has also been reported for the hybrid diamond-chain model, in which the spins of mobile electrons delocalized over decorating quantum dimers (interstitial sites) interact with each other as well as with the localized Ising spins situated at nodal lattice sites [48–52]. The hybrid spin-electron diamond chain with localized Ising spins and delocalized electrons has been exactly solved using
an exact diagonalization procedure in combination with
the decoration-iteration mapping technique. In this class
of models, the competition emerges from the quantum-
mechanical hopping of the interstitial electrons and is
termed as the kinetically-driven spin frustration [48, 49].

While the quantum entanglement has been rather exten-
sively studied in the Ising-Heisenberg diamond chains
[53, 54], it has been almost untouched in the analogous
spin-electron diamond chains. It has been evidenced for
the spin-1/2 Ising-Heisenberg diamond chain that the
ground state is disentangled (classical) when the
Ising coupling between the nodal and interstitial spins
is the predominant one, but it becomes entangled for a
strong enough Heisenberg coupling between the intersti-
tial spins. The quantum concurrence generally decreases
due to thermal fluctuations until it completely vanishes
above a certain threshold temperature. The dependence
of the quantum concurrence on the temperature and ex-
ternal field was explored for example in the Ising-XXZ
[54], as well as Ising-XYZ [55] diamond chain. In the lat-
ter model, the XY anisotropy may result in a re-entrant
behavior of the quantum entanglement.

Although thermodynamic properties of the hybrid
spin-electron diamond chain have been already explored
in some detail [56–58], the inter-relation between the
kinetically-driven spin frustration and the fermionic
quantum entanglement is still missing [59]. In this work,
we will address this question by considering an exactly
solvable diamond chain with localized Ising spins and mo-
bile electrons as a prototype model. The kinetic term
associated with the electron mobility generates compe-
tition and spin frustration. We will report the ground
state phase diagram including ferrimagnetic (FRI), satu-
rated paramagnetic (SPA) and unsaturated paramag-
etic (UPA) phases. We will examine in detail the
magnetization process, which exhibits an intermediate
plateau, as well as the spin correlations around the pla-
quette. A frustrated regime will be characterized by the
absence of a local order that simultaneously satisfy all
first-neighbors correlations. We will also compute the
fermionic quantum concurrence between a pair of inter-
stitial electrons in order to evaluate the influence of ther-
al fluctuations in the degree of quantum entanglement
and its relation with spin frustration. We will unveil dis-
tinct regimes of quantum entanglement as a function of
the hopping amplitude and the external field, including
the emergence of a re-entrant fermionic concurrence in
the vicinity of the zero-temperature FRI-UPA and SPA-
UPA ground-state phase transitions.

This work is organized as follows: In section II, we will
describe the model Hamiltonian and present the method-
ology used to obtain the exact solution for the magneti-
zation, correlation functions and quantum concurrence.
In section II, we present the ground state phase diagram,
and a detailed study of the magnetization processes, cor-
relation functions, spin frustration and quantum entan-
glement. In section IV, we summarize and draw our main
conclusions. Some details of the analytical derivation are
given in the appendices.

II. MODEL AND ITS HAMILTONIAN

Let us consider a coupled spin-electron model on a dia-
mond chain, which contains localized Ising spins $\sigma_i = \pm 1$
on its nodal sites and two mobile electrons on each couple
of interstitial sites (see Fig. 1). For further convenience,
the total Hamiltonian can be defined as a sum over cell
Hamiltonians, i.e. $\mathcal{H} = \sum_i \mathcal{H}_i$, whereas each cell Hamil-
tonian $\mathcal{H}_i$ involves all the interaction terms belonging to
$i$-th diamond unit:

\[
\mathcal{H}_i = -t \sum_{\gamma=\uparrow,\downarrow} \left( c^\dagger_{ij,\gamma} c_{ij,\gamma} + \text{h.c.} \right) - h \sum_{j=1}^2 (n_{ij,\uparrow} - n_{ij,\downarrow}) \\
+ J (\sigma_i + \sigma_{i+1}) \sum_{j=1}^2 (n_{ij,\uparrow} - n_{ij,\downarrow}) \\
- \frac{h}{2} (\sigma_i + \sigma_{i+1}).
\]

Here, $c^\dagger_{ij,\gamma}$ and $c_{ij,\gamma}$ ($j = 1, 2$) are the usual fermionic
creation and annihilation operators for the mobile elec-
trons with the spin $\gamma = \uparrow$ or $\downarrow$ and $n_{ij} = c^\dagger_{ij,\gamma} c_{ij,\gamma}$ is
the respective number operator. The hopping term $t$ takes
into account the kinetic energy related to a quantum-
mechanical hopping of the mobile electrons on the in-
terstitial sites, the coupling constant $J$ accounts for the
nearest-neighbor Ising interaction between the localized
Ising spins and the mobile electrons, and $h$ is Zeeman’s
energy of the localized Ising spins and mobile electrons
in a presence of the external magnetic field.

![FIG. 1: A diagrammatic representation of a correlated spin-
electron model on a diamond chain. The nodal sites are oc-
cupied by the localized Ising spins $\sigma_i = \pm 1$, which are coupled
by the Ising interaction with the spin of mobile electrons hop-
ning between the nearest-neighbor interstitial sites.](image)

The matrix form of the Hamiltonian $\mathcal{H}$ in the local
basis of two mobile electrons for the $i$-th diamond cell
$|\uparrow, \uparrow\rangle_i, |\downarrow, \downarrow\rangle_i, |\uparrow, \downarrow\rangle_i, |\uparrow, 0\rangle_i, |\uparrow, \downarrow\rangle_i, |0, \downarrow\rangle_i$ and
$|\downarrow, \uparrow\rangle_i$ can be
represented as:

$$
\mathcal{H}_i = \begin{pmatrix}
2J\mu_i - 2h & 0 & 0 & 0 & 0 & 0 \\
0 & -2J\mu_i + 2h & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & t & 0 \\
0 & 0 & 0 & 0 & 0 & t \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
$$

(2)

where we have introduced the notation for the total spin of two Ising spins from \(i\)-th diamond unit \(\mu_i = \sigma_i + \sigma_{i+1}\). For simplicity, we have left out the constant term \(-h\mu_i/2\) as it can be later simply added to the corresponding eigenvalues of the Hamiltonian matrix \(\mathcal{H}\). A straightforward diagonalization of the Hamiltonian matrix \(\mathcal{H}\) leads (after taking into account also the constant term \(-h\mu_i/2\)) to the following spectrum of eigenvalues:

$$
\begin{align*}
\varepsilon_{i1} &= 2J\mu_i - 2h - \frac{h}{2}\mu_i, \\
\varepsilon_{i2} &= -2J\mu_i + 2h - \frac{h}{2}\mu_i, \\
\varepsilon_{i3} &= \frac{h}{2}\mu_i + 2t, \\
\varepsilon_{i4} &= -\frac{h}{2}\mu_i - 2t, \\
\varepsilon_{i5} &= \frac{h}{2}\mu_i, \\
\varepsilon_{i6} &= -\frac{h}{2}\mu_i,
\end{align*}
$$

(3-8)

which correspond to the eigenvectors

$$
|\varphi_{i1}\rangle = |\uparrow, \uparrow\rangle_i, \\
|\varphi_{i2}\rangle = |\downarrow, \downarrow\rangle_i, \\
|\varphi_{i3}\rangle = \frac{1}{2}[|\uparrow, \uparrow\rangle_i + |\uparrow, \downarrow\rangle_i + |\downarrow, \uparrow\rangle_i + |\downarrow, \downarrow\rangle_i], \\
|\varphi_{i4}\rangle = \frac{1}{2}[|\downarrow, \uparrow\rangle_i + |\downarrow, \downarrow\rangle_i - |\uparrow, \uparrow\rangle_i - |\uparrow, \downarrow\rangle_i], \\
|\varphi_{i5}\rangle = \frac{1}{\sqrt{2}}[|0, \uparrow\rangle_i - |\uparrow, 0\rangle_i], \\
|\varphi_{i6}\rangle = \frac{1}{\sqrt{2}}[|\downarrow, \uparrow\rangle_i - |\uparrow, \downarrow\rangle_i].
$$

(9-14)

All physical quantities of interest can be subsequently calculated from these exact analytical results by adapting the standard transfer-matrix method.

### A. Magnetization and correlation functions

Here, we will derive exact results for the magnetization and correlation functions, as provided by the transfer-matrix technique. The partition function of the correlated spin-electron model on a diamond chain can be calculated following the procedure:

$$
\mathcal{Z}_N = \sum_{\{\sigma\}} \prod_{i=1}^N \text{Tr}_i e^{-\beta\mathcal{H}_i} = \sum_{\{\sigma\}} \prod_{i=1}^N \frac{e^{-\beta\varepsilon_{ij}}}{\lambda_i^N + \lambda_{i+1}^N}
$$

(15)

where \(\beta = 1/(k_B T)\), \(k_B\) is Boltzmann’s constant, \(T\) is the absolute temperature, the summation \(\sum_{\{\sigma\}}\) is carried out over all possible spin configurations of the localized Ising spins, the symbol \(\text{Tr}_i\) refers to the trace over the degrees of freedom of two mobile electrons from the \(i\)-th diamond unit and \(W = \omega(\sigma_i, \sigma_{i+1}) = \sum_{j=1}^6 e^{-\beta\varepsilon_{ij}}\). The expression \(W\) can be regarded as the transfer matrix:

$$
W = \begin{pmatrix}
\omega(1, 1) & \omega(1, -1) \\
\omega(-1, 1) & \omega(-1, -1)
\end{pmatrix} = \begin{pmatrix}
\omega(2) & \omega(0) \\
\omega(0) & \omega(-2)
\end{pmatrix},
$$

(16)

whereas individual matrix elements depend just on the total spin of two localized Ising spins from \(i\)-th diamond unit according to:

$$
\omega(\mu_i) = \omega(\sigma_i, \sigma_{i+1}) = \sum_{j=1}^6 \exp(-\beta\varepsilon_{ij}) = 2 \exp\left(\beta\frac{h\mu_i}{2}\right) \times [1 + \cosh(2\beta t) + \cosh(2\beta J\mu_i - 2\beta h)].
$$

(17)

The exact result for the partition function \(\mathcal{Z}_N\) then readily follows from the two eigenvalues of the transfer matrix \(W\):

$$
\lambda_{\pm} = \frac{1}{2}[\omega(2) + \omega(-2) \pm Q],
$$

(18)

where \(Q = (\omega(2) - \omega(-2))^2 + 4[\omega(0)]^2\)^{\frac{1}{2}}. In the thermodynamic limit of \(N \to \infty\), only the largest eigenvalue effectively contributes to the partition function.

The unitary transformation that diagonalizes the transfer matrix \(W\), is determined by the matrices \(U\) and \(U^{-1}\):

$$
U = \begin{pmatrix}
\lambda_+ & -\omega(-2) \\
\omega(0) & \lambda_-
\end{pmatrix},
$$

(19)

where \(\lambda_{\pm} = \sqrt{[\lambda_+ - \omega(-2)]^2 + [\omega(0)]^2}\) and \(U^{-1} = U^\dagger\).

Now, one may take advantage of the unitary transformation in order to calculate the magnetization and correlation functions. For instance, the magnetization of localized Ising spins at the nodal lattice sites follows from the relation:

$$
M_\sigma = \langle \sigma_i^\sigma \rangle = \frac{1}{\mathcal{Z}_N} \text{Tr} \left[ \sigma_i^\sigma W^N \right],
$$

(20)
where $\hat{\sigma}^z = U^{-1}\sigma^z U$ and $\hat{W} = U^{-1}WU$. $\sigma^z$ is the standard $2 \times 2$ Pauli matrix associated with the z-component of a nodal Ising spin. A similar formula can also be derived for the magnetization at the interstitial site $j = 1, 2$ of the $i$-th cell:

$$M_S = \langle S^z_{ij} \rangle = \frac{1}{Z_N} \text{Tr} \left[ \hat{S}^z_{ij} \hat{W}^{-N-1} \right],$$

where $\hat{S}^z_{ij} = U^{-1}\Sigma^z_{ij} U$, with the elements $\Sigma^z_{ij}(\sigma_i, \sigma_{i+1}) = \text{Tr} S^z_{ij} e^{-\beta H_i}$ and the trace performed over the states of the interstitial sites belonging to the $i$-th cell. The matrix $S^z_{ij}$ corresponds to the $z$-component of the spin operator at the interstitial site $j = 1, 2$ of the $i$-th cell, written in the corresponding $6 \times 6$ sub-space. The total magnetization can be then obtained either by adding both individual contributions of the localized nodal Ising spins and the mobile electrons, or respectively, from the usual formula:

$$M = -\frac{1}{\beta} \frac{\partial}{\partial \beta} \ln Z_N. \quad (22)$$

The same procedure can be used to calculate the correlation functions. The correlation functions between various spatial components of spin operators $S^z_{ij}$ at the interstitial sites of an elementary plaquette can be calculated as:

$$\langle S^z_{i_1} S^z_{i_2} \rangle = \frac{1}{Z_N} \text{Tr} \left[ \hat{S}^z_{i_1} \hat{S}^z_{i_2} \hat{W}^{-N-1} \right],$$

where $\hat{S}^z_{i_2} = U^{-1}\Sigma^z_{i_2} U$, with the elements $\Sigma^z_{i_2}(\sigma_i, \sigma_{i+1}) = \text{Tr} S^z_{i_1} S^z_{i_2} e^{-\beta H_i}$. The correlation function between the localized Ising spins and the interstitial spins is given by:

$$\langle \sigma_i S^z_{ij} \rangle = \frac{1}{Z_N} \text{Tr} \left[ \hat{\sigma}^z \hat{S}^z_{ij} \hat{W}^{-N-1} \right]. \quad (24)$$

### B. Fermionic entanglement

Quantum entanglement is closely related to non-local correlations present in a quantum system. For two qubits, it can be quantified by the entanglement of formation:

$$E_F = \frac{1}{2} \ln \left( 1 + \sqrt{1 - C^2} \right),$$

where

$$H(x) = -x \log_2(x) - (1 - x) \log_2(1 - x),$$

and $C$ is called the quantum concurrence given by:

$$C = \max \left\{ 0, \sqrt{\Lambda_1} - \sqrt{\Lambda_2} - \sqrt{\Lambda_3} - \sqrt{\Lambda_4} \right\}. \quad (27)$$

Here, $\Lambda_i$ are the eigenvalues of the matrix $R = \rho (\sigma^y \otimes \sigma^y) \rho^* (\sigma^y \otimes \sigma^y)$ sorted in descending order, $\sigma^y$ is the usual Pauli matrix and $\rho$ represents the reduced density matrix for a pair of qubits. Because the entanglement of formation is a monotonous function of the concurrence $C$, one may directly use the concurrence as a measure of quantum entanglement ranging from 0 (no entanglement) up to 1 (maximum entanglement).

In the present model, we will quantify the quantum entanglement in the sub-space of up spins in a given plaquette. Therefore, in the local basis $|0\rangle, |0, \uparrow\rangle, |\uparrow, 0\rangle$ and $|\uparrow, \uparrow\rangle$, the reduced density matrix can be written in the following form

$$\rho_{ij} = \begin{pmatrix} a & 0 & 0 & 0 \\ 0 & x & z & 0 \\ 0 & z^* & y & 0 \\ 0 & 0 & 0 & b \end{pmatrix},$$

whose elements can be directly associated with the following thermal averages:

$$b = \langle n_{i, \uparrow}, n_{i, \downarrow} \rangle,$$

$$x = \langle n_{i, \uparrow} \rangle - \langle n_{i, \downarrow} \rangle,$$

$$y = \langle n_{i, \downarrow} \rangle - \langle n_{i, \uparrow} \rangle,$$

$$a = \langle (1 - n_{i, \uparrow})(1 - n_{i, \downarrow}) \rangle,$$

$$z = z^* = \langle c_{1, \uparrow}^c, c_{2, \downarrow} \rangle.$$

Following the procedure elaborated previously in Ref. [58], one arrives to the following explicit form of the eigenvalues:

$$\Lambda_1 = \left( |\langle n_{i, \uparrow} \rangle - \langle n_{i, \downarrow} \rangle| + |\langle c_{1, \downarrow} c_{2, \uparrow} \rangle| \right)^2,$$

$$\Lambda_2 = \left( |\langle n_{i, \uparrow} \rangle - \langle n_{i, \downarrow} \rangle| - |\langle c_{1, \downarrow} c_{2, \uparrow} \rangle| \right)^2,$$

$$\Lambda_{3,4} = \langle n_{i, \uparrow} n_{i, \downarrow} \rangle (1 - 2 \langle n_{i, \downarrow} \rangle + \langle n_{i, \uparrow} \rangle). \quad (30)$$

According to Eqs. [30], the fermionic concurrence can be calculated from the relation:

$$C = 2 \max \left\{ 0, |\langle c_{1, \downarrow} c_{2, \uparrow} \rangle| \right\} \left( 1 - 2 \langle n_{i, \downarrow} \rangle + \langle n_{i, \uparrow} \rangle \right),$$

which depends on the statistical mean values $\langle c_{1, \downarrow} c_{2, \uparrow} \rangle$, $\langle n_{i, \downarrow} \rangle$ and $\langle n_{i, \uparrow} \rangle$ explicitly given in Appendix B. It is noteworthy that the more general formula [31] for the fermionic concurrence reduces to the simpler formula reported previously by Deng and Gu [58] when considering the particular case $\langle n_{i, \downarrow} \rangle = \langle n_{i, \uparrow} \rangle = 1/2$.

### III. RESULTS AND DISCUSSIONS

Now, let us proceed to a discussion of the most interesting results for the coupled spin-electron diamond chain. For simplicity, our further discussion will be restricted to a particular case with the antiferromagnetic
quantum fluctuations and the Zeeman’s splitting.

A. Ground state

First, we will turn our attention to the ground-state phase diagram shown in Fig. 2 which involves the ferromagnetic (FRI), the saturated paramagnetic (SPA) and the unsaturated paramagnetic (UPA) ground states unambiguously determined by the eigenvectors:

\[
|\text{FRI}\rangle = \prod_{i=1}^{N} |\phi_{1i}\rangle \otimes |\sigma_i = -1\rangle,
\]

\[
|\text{SPA}\rangle = \prod_{i=1}^{N} |\phi_{1i}\rangle \otimes |\sigma_i = 1\rangle,
\]

\[
|\text{UPA}\rangle = \prod_{i=1}^{N} |\phi_{4i}\rangle \otimes |\sigma_i = 1\rangle,
\]

with the corresponding eigenenergies per plaquette:

\[
E_{\text{FRI}} = -4J - h,
\]

\[
E_{\text{SPA}} = 4J - 3h,
\]

\[
E_{\text{UPA}} = -h - 2t.
\]

It can be understood from the eigenvectors (32) that the interstitial spins are aligned into the magnetic field and the nodal spins in opposite to the magnetic field within the FRI ground state, while all nodal as well as interstitial spins are equally aligned into the magnetic field within the SPA ground state. However, the most peculiar spin arrangement can be found within the UPA ground state, where the nodal spins are aligned into the magnetic field but the interstitial spins are subject to a quantum entanglement of two antiferromagnetic and two ionic states as described by the eigenvector (32). The phase UPA originates from a kinetically-driven spin frustration, which is closely connected to the quantum-mechanical hopping of two mobile electrons with opposite spins on the interstitial sites. In agreement with this statement, the nodal spins become effectively decoupled. A high degeneracy can be also found at a triple point given by the coordinates \(t/J = 2.0\) and \(h/J = 4.0\), where all three phases co-exist with a nodal antiferromagnetic phase (see Appendix A).

The local spin arrangements inherent to each individual ground state can be witnessed through the pair correlation functions, which can also give insights into how the spin-spin correlations are affected by thermal fluctuations.

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B. Correlation functions and magnetization

The local spin arrangements inherent to each individual ground state can be witnessed through the pair correlation functions, which can also give insights into how

In Fig. 3 we have plotted, for all available ground states, typical thermal dependences of the transverse correlation function between the interstitial spins \(\langle S_{i1}^x S_{i2}^x \rangle\), the longitudinal correlation function between the interstitial spins \(\langle S_{i1}^z S_{i2}^z \rangle\), the longitudinal correlation function between the interstitial and nodal spins \(\langle \sigma_{i1}^z S_{i1}^z \rangle\) for the set of parameters: (a) \(t/J = 1.5, h/J = 3.0\) (FRI phase); (b) \(t/J = 2.5, h/J = 3.0\) (UPA phase); (c) \(t/J = 1.5, h/J = 5.0\) (SPA phase); (d) \(t/J = 2.0, h/J = 4.0\) (triple point). Notice that spin frustration is present in the low temperature regime above the UPA ground state where only out of three longitudinal spin-spin correlations within the elementary plaquette is negative.

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correlation functions shown in Fig. 3(a) clearly confirm anti-parallel spin alignment between the interstitial and nodal spins and the parallel alignment of interstitial spins within the classical FRI phase, whereas an increase in temperature may be responsible for an up-rise of small transverse (quantum) correlations. It is clear from Fig. 3(b) that the longitudinal correlation between the interstitial spins $\langle S^z_{i1} S^z_{i2} \rangle$ is antiferromagnetic at low but ferromagnetic at high temperatures, which indicates a spin frustration above the UPA ground state according to the concept of temperature-dependent spin frustration [59]. The spin correlations within the interstitial spins do not reach unity due to the presence of strong quantum fluctuations associated with the hopping process. The complete spin alignment of the interstitial and nodal spins relevant to the SPA ground state is evident from the correlation functions depicted in Fig. 3(c), where a small increase in transverse correlation function induced by thermal fluctuations can be also observed. Finally, Fig. 3(d) illustrates the correlation functions exactly at the highly degenerate triple point, at which zero temperature asymptotic limits reach nontrivial values $\langle S^z_{i1} S^z_{i2} \rangle = (5 - \sqrt{5})/20$, $\langle S^z_{i1} S^z_{i2} \rangle = (5 + 3\sqrt{5})/20$ and $\langle \sigma^z_{i1} \sigma^z_{i1} \rangle = (3\sqrt{5} - 5)/10$ (see Appendix A).

The total magnetization. Thermal excitations from the UPA ground state may also give rise to a striking increase of the total magnetization, which occurs due to a spin reorientation of the interstitial rather than the nodal spins (see Fig. 4(b)). Contrary to this, the magnetization of the nodal as well as interstitial spins show only a smooth monotonous decrease with the increasing temperature when starting from the SPA ground state (see Fig. 4(c)). Last but not least, the magnetization curves for the highly degenerate triple point is illustrated in Fig. 4(d). These start from the nontrivial zero-temperature asymptotic values $M_S = (5 + \sqrt{5})/10$, $M_S = \sqrt{5}/5$ and $M = (5 + 2\sqrt{5})/5$ (see Appendix A).

![FIG. 4: Temperature dependence of the single-site magnetization $M_S$ of the interstitial spins, the single-site magnetization $M_0$ of the nodal spins and the total magnetization $M$ per diamond unit for the set of parameters: (a) $t/J = 1.5$, $h/J = 3.0$ (FRI phase); (b) $t/J = 2.5$, $h/J = 3.0$ (UPA phase); (c) $t/J = 1.5$, $h/J = 5.0$ (SPA phase); (d) $t/J = 2.0$, $h/J = 4.0$ (triple point).](image)

Thermal behavior of the total magnetization $M$ per diamond unit (dash-dot-dot lines) is plotted in Fig. 4 along with the single-site magnetization $M_S$ of the interstitial spins (dash-dot lines) and the single-site magnetization $M_0$ of the nodal spins (dash lines). Fig. 4(a) serves in evidence that the rising temperature may facilitate a spin reversal of the nodal spins within the FRI phase, which in turn causes a unusual thermally-induced increase in the total magnetization. Thermal excitations from the UPA ground state may also give rise to a striking increase of the total magnetization, which occurs due to a spin reorientation of the interstitial rather than the nodal spins (see Fig. 4(b)). Contrary to this, the magnetization of the nodal as well as interstitial spins show only a smooth monotonous decrease with the increasing temperature when starting from the SPA ground state (see Fig. 4(c)). Last but not least, the magnetization curves for the highly degenerate triple point is illustrated in Fig. 4(d). These start from the nontrivial zero-temperature asymptotic values $M_S = (5 + \sqrt{5})/10$, $M_S = \sqrt{5}/5$ and $M = (5 + 2\sqrt{5})/5$ (see Appendix A).

![FIG. 5: The field dependence of the magnetization for a few different values of the temperature and two selected values of the hopping term $t/J = 1.5$ and 2.5. The upper panel shows the single-site magnetization of the nodal spins, the central panel the single-site magnetization of the interstitial spins and the lower panel the total magnetization per diamond unit.](image)
between the nodal and interstitial spins (see the inset in Fig. 5(b)). Another magnetization scenario shown in Figs. 5(d)-(f) relates to a discontinuous field-induced transition from the UPA state to the SPA state. It can be clearly seen from Fig. 5(e) that the observed magnetization jump near the saturation field occurs on account of a spin reversal of the interstitial spins. The sudden change in the magnetization of the interstitial spins now evokes a subtle decline of the magnetization of the nodal spins. Altogether, it could be concluded that the magnetization curve always displays a magnetization plateau at one-third of the saturation magnetization even though the microscopic mechanism for a plateau formation may be different.

### C. Spin frustration

It is quite apparent from the eigenvector of the UPA ground state that the quantum-mechanical motion of two mobile electrons on the interstitial sites gives rise to a kinetically-induced spin frustration of the nodal Ising spins at zero temperature. To verify a frustrated character of the nodal spins at finite temperatures one may take advantage of the concept of temperature-dependent frustration, which requires a negative sign for the product of correlation functions along an elementary plaquette implying incapability of the spins to satisfy all underlying spin-spin interactions. The negative sign of the product can be achieved just if the longitudinal correlation function between the interstitial spins is predominantly antiferromagnetic (negative). It has been demonstrated in the previous section that the correlation function indeed changes its sign at a certain temperature when starting from the UPA ground state, whereas the relevant frustration temperature can be regarded as an indicator of the transition from the frustrated regime to the non-frustrated one.

The frustration temperature, as calculated from crossing points of the longitudinal correlation function between the interstitial spins, is plotted in Fig. 6 against the hopping term for a few selected values of the magnetic field. It turns out that the antiferromagnetic correlation develops just for a sufficiently strong hopping term, because the coupled spin-electron diamond chain may become frustrated only within the UPA phase. The frustration temperature accordingly starts at low enough magnetic fields and may be delimiting from above by the displayed curves of frustration temperature.

### D. Fermionic concurrence

Last but not least, we will turn our attention to a discussion of the bipartite quantum entanglement between two mobile electrons located at the interstitial sites of a given plaquette, which will be quantified by the fermionic concurrence calculated according to Eq. (31). The temperature dependence of the fermionic concurrence is depicted in Fig. 7 for several values of the hopping term and two different values of the magnetic field. As it could be expected, the concurrence is zero well within the classical FRI phase as illustrated by the solid line corresponding to at $t/J = 1.0$ in Fig. 7(a). On the other hand, the fermionic concurrence within the fully entangled UPA ground state for $t/J = 3.0$ (dash-dot-dot line) starts from its maximum value and then gradually decreases with increasing temperatures. The special case with the fixed value of the hopping term $t/J = 2.0$ corresponds to the phase coexistence of the FRI and UPA phases at zero temperature (the dashed line) and hence, the zero-temperature limit of the fermionic concurrence is given by the mean value of the disentangled FRI phase and the fully entangled UPA phase. However, the most striking finding concerns with a re-entrant behavior of the fermionic concurrence when the hopping parameter is sufficiently close but slightly below the ground-state boundary between the FRI and UPA phases. Under this condition, the fermionic concurrence starts from zero in agreement with the classical character of the FRI ground state, then it emerges at some lower threshold temperature due to thermal excitations to the UPA phase and finally, it completely disappears at a certain higher threshold temperature (see the dash-dot line for the fixed value $t/J = 1.5$).

It can be understood from Fig. 7(b) that the fermionic concurrence displays qualitatively similar thermal varia-
spin frustration of the nodal spins appears due to the quantum entanglement, because the kinetically-driven mutual correlation between the spin frustration and UPA state.

The threshold temperature for the disappearance of entanglement is induced above the classical FRI or SPA ground state, but still keeps it in a close vicinity of the ground-state boundary with the quantum UPA ground state.

The fermionic quantum entanglement generally lies slightly above the frustration temperature, whereas the threshold temperature for the quantum entanglement always start from the same value of the hopping term, t/J = 0.5.

The system is entangled (disentangled) inside (outside) the area delimited by the displayed lines. The re-entrant behavior indicates that thermal fluctuations favors quantum entanglement in the close vicinity of the FRI-UPA and SPA-UPA ground-state phase boundaries.

The mobile electrons on the interstitial sites are fully entangled just within the UPA phase and hence, it follows that all depicted lines of threshold temperature should start from the ground-state boundary between the UPA-FRI and UPA-SPA phases, respectively. The dependences presented in Fig. S are indeed consistent with this statement and they also provide an independent confirmation of the striking re-entrance when the quantum entanglement is induced above the classical FRI or SPA phase on account of vigorous thermal excitations to the UPA state.

At this stage, it might be quite interesting to study a mutual correlation between the spin frustration and quantum entanglement, because the kinetically-driven spin frustration of the nodal spins appears due to the hopping process of the mobile electrons with opposite spins inevitably underlying the quantum entanglement. Bearing this in mind, the fermionic quantum entanglement could be thus regarded as an indispensable ground for the kinetically-driven frustration of the nodal spins. It actually turns out that the zero-temperature asymptotic value of the threshold and frustration temperature always start from the same value of the hopping term, whereas the threshold temperature for the quantum entanglement generally lies slightly above the frustration temperature at low and moderate temperatures. However, the threshold and frustration temperature might also cross each other at a certain higher temperature as illustrated in Fig. 9(a), which gives evidence that the spin frustration of nodal spins may emerge at higher temper-
ture despite of disentangled character of the interstitial spins. However, we must have in mind that the crossing of the frustration and threshold temperature takes place at a certain temperature, which is however high enough to produce only very weak spin-spin correlations around the elementary plaquette.

IV. SUMMARY AND CONCLUSIONS

In the present work, we have provided a detailed analysis of the relationship between spin frustration and quantum entanglement in a hybrid spin-electron system containing the localized Ising spins and mobile electrons. In particular, we have considered the diamond chain prototype model with the localized Ising spins situated at the nodal lattice sites that interact with two delocalized electrons quantum-mechanically hopping between a pair of the interstitial sites. The model was exactly solved using the transfer-matrix technique. The ground-state phase diagram was shown to be composed of two classical SPA and FRI phases in addition to the one quantum UPA phase, in which the interstitial electrons are quantum-mechanically entangled. The relevant spin-spin correlations around an elementary plaquette were obtained and unveiled a low-temperature frustrated regime in the parameter region corresponding to the UPA ground state. In this regime there is no local spin ordering that satisfies simultaneously all signs of the spin correlations. In the present model frustration results from the quantum hopping process that favors the anti-parallel spin alignment of the interstitial electrons. We have also analyzed the distinct magnetization processes and showed the occurrence of intermediate plateau at one-third of the saturation magnetization. Also, we have found that the spin re-orientation of one sub-lattice (nodal or interstitial spins) observable in a vicinity of the field-induced transition is responsible for a small drop in the magnetization of the complimentary sub-lattice. Finally, we have quantified the degree of fermionic entanglement between two interstitial electrons by computing the quantum concurrence in the spin up sub-space.

The low-temperature asymptotic value of the fermionic concurrence has unambiguously confirmed an existence of the quantum entanglement within the UPA ground state, while it has also demonstrated rather unexpected re-entrant behavior due to thermally activated excitations when the hopping term drives the investigated model towards the disentangled FRI and SPA ground states but still preserves it in a vicinity of the ground-state boundary with the quantum UPA ground state. We have also compared the threshold and frustration temperatures with the goal to bring insight into a mutual relationship between the quantum entanglement and geometric spin frustration. It has been convincingly evidenced that these two physical properties are strongly related yet independent. Besides the conventional entangled-frustrated and disentangled-non-frustrated regimes, we have additionally found entangled-non-frustrated and disentangled-frustrated regimes as well. Although geometric spin frustration and quantum entanglement are closely related features within the present model, this result indicates that thermal fluctuations have distinct influence on these two physical aspects. It would be valuable to have further studies of quantum spin chains with competing interactions to shed additional light of the relevant thermal processes influencing the interplay between spin frustration and quantum entanglement.

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VI. APPENDIX A

At the point of co-existence between the SPA, FRI and UPA phases, their corresponding configurations in a plaquette are also degenerated with a nodal antiferromagnetic phase (NAF). Therefore, in the ground state, cells with either one of these configurations are allowed (see Fig. 10). However, NAF cells can only appear in pairs and only FRI cells can be placed between them. Defining $N_{SPA}$, $N_{UPA}$, $N_{FRI}$, and $N_{NAF}$ as the number of cells in each configuration ($N = N_{SPA} + N_{UPA} + N_{FRI} + N_{NAF}$) the number of possible ways to distribute then along the
maximizing $\Omega$, resulting in FRI cells can be distributed between NAF dimers. The magnetic cells (either SPA or UPA) can be arranged, and accounts for the number of ways NAF dimers and para-
magnetic cells, as well as the relevant correlation functions in each configuration are summarized in table I. The proper aver-
age of these quantities, weighted considering the relative 
weights provides the values reported in the main text.

The values of magnetization of the nodal and interstitial 
sites, as well as the relevant correlation functions in each 
configuration are shown. Their correlation between the 
nodal and interstitial sites $\langle \sigma_i^z \rangle$, interstitial magnetization $\sigma_i^z$, correlation between the 
spin $x$-components $\langle \sigma_i^x \rangle$, between their spin $x$-components $\langle \sigma_i^x \rangle$ and $\langle \sigma_i^x \rangle$, $\langle \sigma_i^x \rangle$.

By exploring the unitary transformation that diagonalizes the transfer matrix $\omega$ (see main text), the density matrix elements result in

$$\rho_{k,l} = \frac{\theta_{k,l}(2) + \theta_{k,l}(-2)}{2\lambda_+} + \frac{2\theta_{k,l}(0)\omega(0)}{Q\lambda_+}$$
$$= \frac{[\theta_{k,l}(2) - \theta_{k,l}(-2)] [\omega(2) - \omega(-2)]}{2Q\lambda_+}.$$ (42)

As a function of the proper reduced matrix, one can readily obtain the thermodynamic averages

$$\langle c_{i1,\uparrow} c_{i2,\uparrow} \rangle = 2\rho_{5,4}$$
$$\langle n_{i1,\uparrow}, n_{i2,\uparrow} \rangle = \rho_{1,1}$$
$$\langle n_{i1,\uparrow} \rangle = \rho_{1,1} + 2\rho_{3,3}$$

where the identities $\rho_{5,4} = \rho_{6,3}$ and $\rho_{3,3} = \rho_{4,4}$ were used.

From the above expressions, the quantum concurrence can be explicitly written as

$$C = \max \left\{ 0, 4\rho_{5,4} - 2\sqrt{\rho_{1,1}(1 - \rho_{1,1} - 4\rho_{3,3})} \right\}$$ (44)
