Quasi-1d quantum helimagnets: The fate of multipolar phases

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Coupled frustrated spin-1/2 chains in high magnetic fields described within the ferro- antiferromagnetic \( J_1 - J_2 \) Heisenberg model are studied by DMRG, hard core boson, and spin wave theory approaches. Multipolar phases related to magnon bound states are destroyed (supported) by weak antiferromagnetic (ferromagnetic) interchain couplings \( J_{\text{ic}} \). We show that quantum spin nematics might be found for LiV\( \text{CuO}_4 \) whereas for Li(Na)\( \text{CuO}_2 \) it is prevented by a sizeable antiferromagnetic \( J_{\text{ic}} \). Also for Li\( \text{ZrCuO}_4 \) with a small antiferromagnetic \( J_{\text{ic}} \) expected tricatic or quartic phases are unlikely, too. The saturation field is found to be strongly affected even by a relatively small \( J_{\text{ic}} \).

The frustration of magnetic interactions allows for new phenomena to emerge. Some spin-chain compounds are frustrated magnets in, for instance, the case of ferromagnetic (FM) nearest neighbor (NN) exchange interaction \( (J_1) \) competing with an antiferromagnetic (AFM) next-neighbor (NNN) one \( (J_2) \). Recent theoretical studies indicate that in a high magnetic field, such a \( J_1-J_2 \) chain can display e.g. nematic quasi long-range order for certain \( \alpha = -J_2/J_1 \) \cite{3,5}. This nematic state might be thought of as a condensate of two-magnon bound states \( \mathbf{6} \). Depending on the value of \( \alpha \) also three- or four-magnon bound states might condense, resulting in a very rich phase diagram with exotic magnetic multipolar (MMP) phases. However, to establish whether these MMP phases can be realized in a real material it is essential to determine their robustness, i.e. the very existence of multimagnon bound states (MBS) with respect to various interchain (IC) couplings \( J_{\text{ic}} \), which can be (very) small for certain spin-chain compounds, but that is always present, and, as we will show here can be detrimental. Such a transition from 1D to 2D or 3D can be non-trivial. In particular, from quantum mechanics it is well-known that bound states are strongly pronounced in 1D and more rare in 2D or 3D. To understand quantitatively the role of IC the question arises in which cases even a relatively weak IC is still important or even crucial? Here we address such a problem, namely, the fate of MMP states, such as the nematic spin state related to MBS at high magnetic fields and consider the spin-1/2 frustrated isotropic \( J_1-J_2 \)-Heisenberg model mentioned above supplemented by various IC \cite{17}. Recently, the 1D-model and related compounds revealed considerable interest \cite{2,8,9,10,11,12,13,14,15}. Nowadays it is the most popular model for edge-shared chain cuprates (see e.g. \cite{2}). Additional AFM couplings typically provided by the IC enhance the kinetic energy of magnons. Hence, AFM(FM) IC may hinder(favor) the formation of low-lying MBS. A FM IC may create even new MMP states. An examination of real Q-1D systems to predict the changes due to finite \( J_{\text{ic}} \) and to evaluate the chances to detect MMP states in certain compounds is of broad interest \cite{6,16,20,25,26}.

Among edge-shared cuprates LiCu\( _2 \)O\( _2 \), the isomor-
phic NaCu$_2$O$_2$, and LiVCuO$_4$\textsuperscript{27} (see Fig. 11 for comparison the reference systems Li$_2$CuO$_2$ and Ca$_2$Y$_2$Cu$_2$O$_{10}$ with strong IC are shown, too) have been proposed to be candidates for quantum-spin nematics, i.e. quadrupolar phases derived from 2-MBS. Systems like Li$_2$ZrCuO$_4$ \textsuperscript{12, 22} located closer to the FM-spiral critical point might be candidates for the tricatic or quartic MMP. Besides the strength also the influence of various IC topologies resulting from different arrangements of individual chains is of interest. Various types of IC are shown in Fig. 11. The simplest case is given by unshifted neighboring chains and a predominant perpendicular $J^\perp_{ic}$. Here spirals on NN chains are only weakly affected by an AFM IC \textsuperscript{10} (classically their pitch angle, i.e. the incommensurate (INC) inchain magnetic structure in the dipolar phase at ambient external fields remains even unaffected). Hereafter, we call this IC the 'unfrustrated IC'.

An effective 2D arrangement of the magnetically active Cu$^{2+}$-sites is realized approximately for Li$_x$(Na)$_{1-x}$Cu$_2$O$_2$, where $J_{ic} \sim (0.5$ to 1)$J_0 \sim 40$ to 100 K \textsuperscript{28, 30}. A square lattice of unshifted chains, i.e. the 3D case considered in Ref. 24 might be realized in LiVCuO$_4$, if the IC denoted as $J_3$ in Ref. 23 is dominant as compared with the IC in the (ab)-plane (see middle of Fig. 1). Another 3D case but with shifted adjacent chains is realized for Li$_2$CuO$_2$ (see Fig. 1) for which $H_s$ has been found recently \textsuperscript{18}. $J_{ic} \approx 10$ K can be extracted from $H_s(0)$, from inelastic neutron scattering studies, and from bandstructure results \textsuperscript{17}. The same order holds also for Li$_2$ZrCuO$_4$ where buckling of the CuO$_2$ chains reduces $J_{ic}$ \textsuperscript{14}.

We used the density-matrix renormalization group (DMRG) method \textsuperscript{31} with imposing periodic boundary conditions (PBC) for all directions. In general, it is known that this method is much less appropriate for $D > 1$. However, spin systems with up to about $\sqrt{10} \times \sqrt{10} \times L = \sqrt{10} \times \sqrt{10} \times 50$ sites can be studied by taking a proper construction of the lattice block (see Ref. 18). We kept $m \approx 800 - 4000$ density-matrix eigenstates in the renormalization procedure. In fact, about 100 - 300 sweeps are necessary to obtain the GS energy within a convergence of $10^{-7}J_1$ for each $m$ value. All calculated quantities were extrapolated to $m \rightarrow \infty$ and the maximum error in the GS energy is estimated as $\Delta E /J_1 \sim 10^{-4}$, while the discarded weight is less than 1 $\times 10^{-6}$. Under the PBC, a uniform distribution of individual chains is of interest. Various types of IC are proposed to be candidates for quantum-spin nematics, i.e. quadrupolar phases derived from 2-MBS. Systems like Li$_2$ZrCuO$_4$ \textsuperscript{12, 22} located closer to the FM-spiral critical point might be candidates for the tricatic or quartic MMP. Besides the strength also the influence of various IC topologies resulting from different arrangements of individual chains is of interest. Various types of IC are shown in Fig. 11. The simplest case is given by unshifted neighboring chains and a predominant perpendicular $J^\perp_{ic}$. Here spirals on NN chains are only weakly affected by an AFM IC \textsuperscript{10} (classically their pitch angle, i.e. the incommensurate (INC) inchain magnetic structure in the dipolar phase at ambient external fields remains even unaffected). Hereafter, we call this IC the 'unfrustrated IC'.

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We start with the simplest IC case of parallel chains within a plane (2D) or within a square-lattice arrangement of chains (3D) and a single perpendicular IC $J_{ic} = J_{ic} /|J_1|$ vs. inchain frustration (d,e), where $N_{ic} = 4$ is the number of nearest interchain neighbors. The phase boundaries are constructed from the 'kinks' in $h_s$-plots like in (a-c). The contour lines in (d) show the values of $h_s$. The 2D case with $N_{ic} = 2$ is shown also in (d,e) (dotted lines).

FIG. 2: (Color) Upper (a-c): Saturation field vs IC; lower: critical IC for the 3D case with perpendicular IC $j_{ic} = N_{ic} J_{ic} /|J_1|$ vs. inchain frustration (d,e), where $N_{ic} = 4$ is the number of nearest interchain neighbors. The phase boundaries are constructed from the 'kinks' in $h_s$-plots like in (a-c). The contour lines in (d) show the values of $h_s$. The 2D case with $N_{ic} = 2$ is shown also in (d,e) (dotted lines).
A relation $G = |J_1|f(\alpha)$ is valid also in other regimes, where $f$ is a simple function affected by the type of the IC and the region of the MMP phase diagram. In the 1-magnon regimes valid for Li$_2$CuO$_2$ and Ca$_2$Y$_2$Cu$_5$O$_{10}$ (see below) we have $f = 2(1 - \alpha)$ [18]. For the nematic phase in full accord with the DMRG we obtained numerically exact values of $h_s$ using the hard-core boson approach [19]. Expanding the 2-particle Green’s function in powers of $j_c$ we arrive at analytical expressions:

$$h_s(\alpha) \approx h_s^\text{IC}(\alpha) + \tilde{j}_c/2 + N_c \eta(\alpha) j_c^2 + O(j_c^4),$$

$$h_s^\text{IC}(\alpha) = 2\alpha - 1 + 0.5/(1 + \alpha),$$

where $\eta(\alpha) = (1 + \alpha)(3\alpha^2 + 3\alpha + 1)/(2[1 + 2\alpha^2]) \approx 5/3 + 3\alpha/2$ . The expansion coefficients for higher order terms differ for $D=2$ and 3 reflecting subtle natural differences in the quantum fluctuations. A detailed discussion will be given elsewhere. Comparing the Eqs. (1) and (3) we stress the presence of nonlinear IC terms and two times smaller linear term in the nematic phase as compared with the usual one-magnon phase. The inspection of Figs. 2(d,e) shows that the critical IC of the nematic region reaches a maximum as a function of $\alpha$. Its position $\alpha \approx 1.103$ and height $j_c/4 \approx 0.071688$ are close to the feature shown in Fig. 6 of Ref. 24.

Keeping the linear IC term in Eq. (3) we arrive at

$$g\mu_B H_s + 2\Theta_{\text{cw}} = K = |J_1|\left[\alpha + 0.5/(1 + \alpha)\right].$$

Thus, $G$ and $K$ composed from IC affected quantities depends itself on single chain properties, only. In most cases it is easier to determine the latter theoretically whereas $G$ or $K$ can be found from experiment.

Applying Eq. (2) to Li$_2$ZrCuO$_4$ we predict $\Theta_{\text{cw}} = 93.3$ K for a preliminary experimental value of $H_s$ of about 13 T [32] using $J_1 = 273$ K, $\alpha = 0.29$ to 0.3 [12]. The small 1D-value of $H_s \approx 4.2$ to 5.9 T, only, clearly shows the importance of $J_{ic}$ in the vicinity of the critical point where $H_s \to 0$. The validity of Eq. (2) is guaranteed by $j_c = 0.0264756$ (i.e. 7.2 K) to 0.023659 (i.e. 6.5 K) exceeding well $j_c = 0.009539$ to 0.013458 deduced from the 2D-phase diagram. The $j_{ic,c}$ would allow $H_s = 6.2$ T to 8.9 T in the tricatic phase at most. The estimated weak IC given above is close to L(S)DA+$U$ results [14]. Thus, we are clearly outside the tricatic or quartic phases and deep enough in the usual dipolar phase. The 1-magnon picture holds also for Li(Na)Cu$_2$O$_2$ where $j_{ic,c}$ for the nematic phase is exceeded by a factor of four. In fact, from the LDA derived $J_{ic}$ and $J_1$ we estimate $j_c \approx 0.7$ well above 0.170 $J_{ic,c} = 0.1704$ taken from Fig. 2 for $\alpha \approx 1$ for LiCu$_2$O$_2$ [28]. Similarly, using the empirical values for NaCu$_2$O$_2$: $\Theta_{\text{cw}} = -41$ K taken from the 1/\chi(T) data at $350 \leq T \leq 400$ K, $\alpha = 1.9$, $J_1 \approx -48$ K, and $q_a = 2.06$, we predict $H_s \approx 155$ T. From Eq. (1) we estimate $j_c \approx 0.73$ well above $j_{ic,c} \approx 0.172$ (see Fig. 2) and again close to LDA-results [30].

Now we turn to the case of diagonal IC as in Li$_2$CuO$_2$ (see Fig. 1). For a strong enough IC the MBS are suppressed and only 1-magnon excitations survive at high fields (see Fig. 4(b)). Then $h_s$ reads

$$h_s = g\mu_B H_s/|J_1| = \tilde{j}_c + j_c^* \frac{j_c}{j_{ic}} \text{ if } j_c \geq j_{ic}^*, \tilde{j}_c = N_c j_c \ (6)$$

![FIG. 3: (Color) Magnetization vs. applied external field for a 2D arrangement of chains with a direct AFM IC as modelled by four chains with $N = 24$ sites in each chain for different IC $j_c \equiv J_c/|J_1|$ and an inchain frustration $\alpha = 1/2$. Note that each point shown represents a step. The critical value of $j_c/2$ amounts 0.088 for $D=3$ and 0.094 for $D=2$.](image)

![FIG. 4: (Color) 3D phase diagrams for diagonal IC. $h_s$ (given by contour lines) as a function of the normalized IC $j_c$ and the inchain frustration $\alpha$. Lower(Upper): (un)shifted chains with $\pm 3b/2$ ($\pm b$) IC, where $b$ is the inchain Cu-Cu distance.](image)
where \( N_a = 8 \). Eq. (6) is valid for \( j_{ic}(\alpha) > (4\alpha - 1)/9 \equiv j_{ic}^* \), for \( j_{ic}^* = 0 \). We obtained from INS data [2]: \( J_{ic} \approx 9K > J_{ic}^*/(0.332) = -0.0364J_1 \approx 8.2 \) K. Then \( H_s \) depends solely on the IC which can be directly read off from \( H_s(T = 0) \) [8]. For weaker IC \( H_s \) depends also somewhat on \( \alpha \). Our results also suggest that in this intermediate INC-phase above a second critical IC \( j_{ic}^* = 0 \) only specific INC 1-magnon low-energy excitations exist, see Fig. 4. Below \( j_{ic}^* \), 3-MBS are recovered as low-energy excitations and only this narrow region is 1D-like. The commensurate (C) phase behaves like an ordinary 3D antiferromagnet despite its seemingly quasi-1D nature. For unshifted NN chains (see Fig. 1), the C-phase is missing. There is only one critical IC separating INC 1-magnon excitations from 3-MBS.

Generally, \( \theta = -2\Theta_{cw}/J_1 \) provides a useful constraint

\[
1 = \alpha + \beta + \theta + (D - 1)\left[ j_{ic,1} + 2 \sum_j j_{ic,t} \right],
\]

(7)

for the exchange integrals, where in addition to \( \alpha \) further inchain and IC quantities \( \beta = -J_3/J_1 \), \( j_{ic,1} = -J_{ic,1}/J_1 \), and \( j_{ic,t} = -J_{ic,t}/J_1 \) for various diagonal couplings have been introduced. From Eq. (7) a stringent constraint for \( \alpha \) for LiVCuO$_4$ follows. From \( 1/\chi(T) \) at 500 K \( T \leq 650 \) K a small FM value \( \Theta_{cw} \approx 7.4 \) K can be fitted from the data shown in Refs. [24, 33]. The FM ordering of spins observed by neutron diffraction can be maintained both by a FM inplane and a perpendicular AFM 3D IC (see Fig. 1). Then we may assume for the sake of simplicity that both IC almost cancel in Eq. (7) and ignore the small terms \( \beta, \) and \( j_{ic} \) in zeroth approximation. The weakness of the total IC is suggested also by the weak magnetic moment \( m = \mu_0J_1 \) at \( T = 0 \) [34] pointing to strong quantum fluctuations. A first estimate [33] of the dispersion of the INS peaks as well as of the INS intensity above 10 meV yields a reasonable description for \( \alpha = 0.8 \) and \( J_1 = -73.2 \) K and \( J_3 = -0.07 \) K as suggested by a mapping of a five-band Hubbard model (exact diagonalizations) for a CuO$_2$O$_2$ cluster onto a six-site \( J_1-J_2-J_3 \)-Heisenberg ring. Hence, we conclude, that for \( \alpha \approx 0.85 \pm 0.1 \) and \( J_1 \approx -80 \) K nematics could be observed in LiVCuO$_4$.

Using Eq. (3) we see that this is also in reasonable accord with the experimental \( H_s \)-data [24, 25] since our 1D set gives for the above mentioned rough estimate about 48 T for \( g = 2 \) and \( H \) directed along the hard axes and about 42 T for the weak axis with \( g = 2.3 \). Note that our \( J \)'s differ strongly from those given inappropriately in Refs. [25, 26]. The latter have been employed unfortunately in Refs. [6, 20] as ‘empirical’ input parameters. More detailed studies including explicitly the IC are necessary to refine all \( J \)'s. In particular, the quantum effect of \( J_1 \) on the pitch angle is of interest. A more detailed study of FM IC as well as of the \( J_1-J_2-J_3 \) inchain model will be considered elsewhere. A challenging point is also to find MP phases beyond the 2-magnon Bose condensation [6] triggered by a FM IC.

To summarize, the crucial role of realistic AFM IC in Q-1D helimagnets has been demonstrated. The rich and exotic physics of multipolar phases recently predicted for single chains is very sensitive to the strength of the IC. It can be readily eliminated by a weak AFM IC especially for triatic, quartic, etc. phases. For most CuO$_2$ chain systems studied so far, except probably LiVCuO$_4$, where a nematic phase or some other exotic phase might be expected, the AFM IC is too strong to allow for multipolar phases. The examination of various weak FM IC as well as of anisotropy effects in real materials is under study.

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Note that the ordered moment for LiV\textsubscript{Cu}O\textsubscript{4} is three times smaller than that for Li\textsubscript{2}CuO\textsubscript{2} or Ca\textsubscript{2}Y\textsubscript{2}Cu\textsubscript{5}O\textsubscript{10}.