Noncollinear Magnetic Order Stabilized by Entangled Spin-Orbital Fluctuations

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Quantum phase transitions in the two-dimensional Kugel-Khomskii model on a square lattice are studied using the plaquette mean field theory and the entanglement renormalization ansatz. When $3z^2 - r^2$ orbitals are favored by the crystal field and Hund’s exchange is finite, both methods give a noncollinear magnetic order which follows from further neighbor spin interactions trig-

\[ S = \frac{1}{2} \] spins, as in the three-dimensional (3D) Kugel-Khomskii (KK) model [12, 13], and lead to a spin-orbital liquid phase [15], with examples on a triangular lattice in $e_g$ (LiNiO$_2$ [16]) and $t_{2g}$ (LiNiO$_2$ [17]) orbital systems. Frustrated spin-orbital interactions to further neighbors may also destabilize long-range magnetic order [18]. An opposite case when orbital excitations determine the spin order was not reported until now.

The phase diagram of the 3D KK model remains controversial in the regime of strongly frustrated interactions — it has been suggested that either spin-orbital fluctuations destabilize long-range spin order [12] or an orbital gap opens and stabilizes spin order [13]. This difficulty is typical for systems with spin-orbital entanglement [19] which may occur both in the ground state [20] and in excited states [21]. The best known examples are the 1D [22] or two-dimensional (2D) [23] SU(4) models, where spin and orbital operators appear in a symmetric way.

Instead, the symmetry in the orbital sector is much lower and orbital excitations measured in KCuF$_3$ [24] are expected to be inherently coupled to spin fluctuations [25].

In this Letter we present a surprising noncollinear spin order in the 2D KK model which goes beyond mean field (MF) studies [26], and explain its origin. So far, non-collinear spin order was obtained for frustrated exchange in Kondo-lattice models on square lattices, without [27] and with [28] orbital degeneracy, or at finite spin-orbit coupling [29]. In MnV$_2$O$_4$ spinel it is accompanied by a structural distortion and the orbital order [30]. Here we find yet a different situation — when frustrated nearest neighbor (NN) exchange terms almost compensate each other and orbitals are in ferro-orbital (FO) state, the spin order follows from further neighbor spin interactions trig-

\[ t \ll U \] and charge fluctuations are suppressed. On the one hand, spin degrees of freedom may separate from the orbitals when the coupling to the lattice is strong, as in LaMnO$_3$ [11] and recently shown to happen also in KCuF$_3$ [11]. On the other hand, the spin-
orbital quantum fluctuations are strongly enhanced for low $S = \frac{1}{2}$ spins, as in the three-dimensional (3D) Kugel-Khomskii (KK) model [12, 13], and lead to a spin-orbital liquid phase [15], with examples on a triangular lattice in $e_g$ (LiNiO$_2$ [16]) and $t_{2g}$ (LiNiO$_2$ [17]) orbital systems. Frustrated spin-orbital interactions to further neighbors may also destabilize long-range magnetic order [18]. An opposite case when orbital excitations determine the spin order was not reported until now.

Introduction.— Almost 40 years ago Kugel and Khomskii realized that spins and orbitals should be treated on equal footing in Mott insulators with active orbital degrees of freedom [1]. Their model explains qualita-

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a variational ansatz in a form of a product of plaquette $2 \times 2$ wave functions $\mathcal{P}$’s [33]. Energy is minimized with respect to $\mathcal{P}$’s to obtain the best approximation to the ground state. ERA is a refined version of the PMF, where the product of $\mathcal{P}$’s is subject to an additional unitary transformation, being a product of $2 \times 2$ “disentanglers” $\mathcal{U}$. They introduce entanglement between different plaquettes and make ERA more accurate.

Kugel-Khomskii model and methods.— The perturbation theory for a Mott insulator with active $e_g$ orbitals in the regime of $t \ll U$ leads to the spin-orbital model [34], with the Heisenberg SU(2) spin interactions coupled to the orbital operators for the holes in the $d^0$ ionic states,

\[
\mathcal{H} = -\frac{1}{2} J \sum_{\langle ij \rangle|\gamma} \left( r_1 \Pi_{ij}^{(ij)} + r_2 \Pi_{ij}^{(ij)} \right) \left( \frac{1}{2} - \tau_i^\gamma \tau_j^\gamma \right) + (r_3 + r_4) \Pi_{ij}^{(ij)} \left( \frac{1}{2} - \tau_i^\gamma \right) \left( \frac{1}{2} - \tau_j^\gamma \right) + \mathcal{H}_0, \tag{1}
\]

Each bond $\langle ij \rangle$ connects NN sites $\{i,j\}$ along one of the orthogonal axes $\gamma = a, b$ in the ab plane. The model describes the spin-orbital superexchange in $\text{K}_2\text{CuF}_4$ [33], with the superexchange constant $J = 4t^2/U$. The coefficients $r_1 \equiv 1/(1 - 3\eta)$, $r_2 \equiv 1/(1 - \eta)$, $r_3 \equiv 1/(1 + \eta)$, and $r_4 \equiv 1/(1 + 3\eta)$ refer to the $d^0_d^0$ charge excitations to the upper Hubbard band [33] and depend on Hund’s exchange parameter

\[
\eta = \frac{J_H}{U}. \tag{2}
\]

The spin projection operators $\Pi_{ij}^\gamma$ and $\Pi_{ij}^{(ij)}$ select a singlet ($\Pi_{ij}^\gamma$) or triplet ($\Pi_{ij}^{(ij)}$) configuration for spins $S = 1/2$ on the bond $\langle ij \rangle$, respectively,

\[
\Pi_{ij}^{(ij)} = \left( \frac{1}{4} - S_i \cdot S_j \right), \quad \Pi_{ij}^{(ij)} = \left( \frac{3}{4} + S_i \cdot S_j \right). \tag{3}
\]

Here $\tau_i^\gamma$ act in the subspace of $e_g$ orbitals occupied by a hole $\langle \{x\}, |z\rangle \rangle$, with $|\gamma \rangle \equiv (3x^2 - r^2)/\sqrt{6}$ and $|x\rangle \equiv (x^2 - y^2)/\sqrt{2}$. They can be expressed in terms of Pauli matrices $\sigma_{\gamma}^i$, $\sigma_{\gamma}^j$ in the following way [33]:

\[
\tau_i^{\alpha(b)} = \frac{1}{4} \left( -\sigma_i^z \pm \sqrt{3} \sigma_i^\gamma \right), \quad \tau_i^{c} = \frac{1}{2} \sigma_i^z. \tag{4}
\]

The term $\mathcal{H}_0$ in Eq. (1) is the crystal field splitting of two $e_g$ orbitals induced by the lattice geometry or pressure,

\[
\mathcal{H}_0 = -E_z \sum_i \tau_i^c. \tag{5}
\]

When $|E_z| \gg J$ it dictates the FO order with either $z$ or $x$ orbitals as long as we stay in the AF regime. This ground state can be further improved using perturbation theory in a dimensionless parameter $|E_z|^{-1} \equiv J/|E_z|$

In the PMF one finds self-consistently MFs: $s_i^\alpha \equiv \langle S_i^\alpha \rangle$, $t_i^\gamma \equiv \langle \tau_i^\gamma \rangle$, and $v_i^{\gamma,\gamma} \equiv \langle S_i^\gamma \tau_i^\gamma \rangle$. Here $\gamma = a, b$, $\alpha = x, z$,

\[
\begin{align*}
E_{12} & 
\begin{align*}
AF & \quad t''=1/2 \\
AF & \quad t''=-1/2 \\
FM & \quad t''=1/2 \\
FM & \quad t''=-1/2 \\
PM & \quad \text{PVB} \\
PM & \quad \text{ortho-AF}
\end{align*}
\end{align*}
\]

Figure 2. (color online). Phase diagram of the 2D KK model in the PMF (solid lines) and ERA (dashed lines) variational approximation. Insets show representative spin and orbital configurations on a $2 \times 2$ plaquette — $x$-like ($t'' = \frac{1}{2}$) and $z$-like ($t'' = \frac{-1}{2}$) orbitals [36] are accompanied either by AF spin order (arrows) or by spin singlets in the PVB phase (ovals). The FM phase has a two-sublattice AO order with $t'' = \frac{1}{2}$ at $E_z = 0$ or FOz order (FM2). In between the AF and FM (FM2) phase on finds an exotic ortho-AF phase — it has a noncollinear spin order, see text.
while finite \( E_z \) induces transverse polarization \( \langle \sigma^z \rangle \neq 0 \).

The phase diagram includes also two AF phases. They have uniform FO order with \( \langle \sigma^z \rangle > 0 \) for \( E_z > 0 \) and \( \langle \sigma^z \rangle < 0 \) for \( E_z < 0 \). The spin interactions in two AF phases are nonequivalent and are much weaker for \( E_z < 0 \) than for \( E_z > 0 \) — this difference increases up to a factor of 9 for fully polarized orbitals [11]. These two phases are separated by the plaquette valence bond (PVB) phase with pairs of parallel spin singlets, horizontal or vertical and alternating between NN plaquettes. Note that the PVB phase is an analog of spin liquid phases found before frustrated Kondo lattice models [43]. To explain the exotic magnetic order in the ortho-AF phase shown in Fig. 3 we derive an effective spin model Eq. (6) follows.

The first order yields the Heisenberg Hamiltonian

\[
H_{s}^{(1)} = \frac{1}{25} (-3r_{1} + 4r_{2} + r_{4}) \sum_{\langle ij \rangle} (S_{i} \cdot S_{j} ).
\]  

(7)

The NN interaction \( J_{1} \equiv (-3r_{1} + 4r_{2} + r_{4})/25 \) changes sign at \( \eta_{0} \approx 0.155 \) implying a direct AF-FM transition. However, this turns out to be a premature conclusion because the vanishing of \( H_{s}^{(1)} \) at \( \eta_{0} \) makes higher order terms in Eq. (6) relevant. Indeed, \( \eta_{0} \) nicely falls into the ortho-AF area of the phase diagram in Fig. 2 where the NN interaction \( J_{1} \) is small and frustrated.

Higher order terms. — Higher order terms arise by flipping orbitals from the ground state |0⟩. Given that \( V \) has non-zero overlap only with states having one or two NN orbitals flipped from \( z \) to \( x \), one finds in second order

\[
H_{s}^{(2)} = \frac{\xi(\eta)}{|\varepsilon_{z}|} \left\{ \sum_{\langle ij \rangle} (S_{i} \cdot S_{j} ) - \frac{1}{2} \sum_{\langle\langle ij \rangle\rangle} (S_{i} \cdot S_{j} ) \right\} ,
\]  

(8)

with \( \xi(\eta) = (r_{1} + 2r_{2} + 3r_{4})^{2}/2^{10} \). Here \( \langle ij \rangle \) and \( \langle\langle ij \rangle\rangle \) stand for NN and 3NN sites \( i \) and \( j \), see Fig. 1(a) for the origin and sign of these interactions. Apart from this, the second order also brings the \( |\varepsilon_{z}|^{-1} \) correction to the Heisenberg interactions of \( H_{s}^{(1)} \) [7], moving the transition point from \( \eta_{0} \) to \( \eta_{0} + O(\varepsilon_{z}^{-1}) \).
\[ \alpha = \text{terpenetrating classical antiferromagnets} \]

The NNN AF interaction in \( H_s^{(2)} \) alone would give two quantum antiferromagnets on interpenetrating sublattices \([44]\), but the additional 3NN FM term makes these AF states more classical than in the 2D Heisenberg model \([45]\). This “double-AF” configuration is already similar to the ortho-AF phase in Fig. 3. However, the second order does not explain why the spins in the ortho-AF phase prefer to be orthogonal on NN bonds, and we have to proceed to the third order.

The third order in Eq. 6 produces many contributions to the spin Hamiltonian, but we are interested only in qualitatively new terms compared to the lower orders. The terms bringing potentially new physics are the ones with connected products of three different Heisenberg bonds \([44]\). The final result is a four-spin coupling,

\[
H_{\perp}^{(3)} = \frac{1}{\varepsilon_2} \chi(\eta)\xi(\eta) \sum_{(ij)||\gamma} (S_i \cdot S_j) (S_{N_i(i)} \cdot S_{N'(j)}),
\]

where \( \gamma = -\gamma \) and \( S_{N_i(i)} \equiv \sum_{\alpha \neq \gamma} s_\alpha S_i + \alpha \) is an effective spin around site \( i \) in the direction \( \gamma \), see Fig. 4(b). Here \( \chi(\eta) = 9(r_1 + r_4)/2^7 \), \( \alpha \in \{\pm a, \pm b\} \), and \( s_\alpha = -1 \) for \( \alpha = \pm b \) and \( s_\alpha = 1 \) otherwise. In the limit of two interpenetrating classical antiferromagnets \( H_{\perp}^{(3)} \) gives the energy per site, \( \varepsilon_{\perp}^{(3)} \approx \varepsilon_2^2 \chi(\eta)\xi(\eta)(\frac{3}{2} \cos \varphi)^2 \), where \( \varphi \) is an angle between the NN spins \([45]\). This classical energy is minimized for \( \varphi = \pi/2 \) which explains the exotic magnetic order in the ortho-AF phase, shown in Fig. 3.

Spin-orbital entanglement.— The ground state \( |AF_\perp\rangle \) of \( H_s \) is nearly classical, except for small quantum corrections obtained within the spin-wave expansion \([45]\).

Thus one might expect that the spins are not entangled with orbitals. However, this argument overlooks that the resulting spins in \( H_s \) are dressed with orbital and spin-orbital fluctuations. Indeed, within the perturbative treatment we obtain the full spin-orbital ground state,

\[
|\Psi_{SO}\rangle \propto \left(1 - \sum_{n \neq 0} \frac{V_n}{\varepsilon_n} + \sum_{n,m \neq 0} \frac{V_n V_m}{\varepsilon_n \varepsilon_m} - \ldots\right) |\Phi_0\rangle,
\]

where \( V_n \equiv |n\rangle \langle n|, V_n \varepsilon_n \) are excitation energies, and \( |\Phi_0\rangle \equiv |AF_\perp\rangle(0) \) is the disentangled classical state (Fig. 3). The operator sum in front of \( |\Phi_0\rangle \) dresses this state with both orbital and spin-orbital fluctuations. When the purely orbital fluctuations are neglected and density of spin-orbital defects is assumed to be small, one finds

\[
|\Psi_{SO}\rangle \simeq \exp \left(-\frac{1}{\varepsilon_z} \sum_{(ij)||\gamma} D_{ij}^\gamma \right) |\Phi_0\rangle,
\]

where

\[
D_{ij}^\gamma = \{-A \sigma_i^x \sigma_j^x + B (\sigma_i^x + \sigma_j^x) s_z \} \Pi_{ij}^{(3)}
\]

is the spin-orbital excitation operator on the bond \( (ij) \), with \( A = 3(r_1 + r_4)/2^9 \) and \( B = \sqrt{3}(r_1 + 2r_2 + 3r_4)/2^9 \). Both terms in Eq. 12 project on a NN spin singlet, but the first one flips two NN orbital while the second one generates only one flipped orbital. In short, the exponent \( e^{-D_{ij}^\gamma/\varepsilon_z} \) dresses the classical ortho-AF state \( |AF_\perp\rangle \) in Fig. 3 with the entangled (spin-singlet/flip-orbital) defects, see Fig. 4. The density of such entangled defects increases when \( |\varepsilon_z| \) is decreased towards the PVB phase.

Topological defects.— The order parameter of the ortho-AF phase has non-trivial topology. The ground state is degenerate with respect to different orientations of its order parameter that consists of two orthogonal unit vectors defining orientation of each antiferromagnet. The first vector lives on the whole sphere \( S^2 \), but the second one is restricted to a circle \( S^1 \) because it is orthogonal to the first. In addition to spin-wave excitations, this \( S^2 \times S^1 \) topology allows for skyrmions (textures) \([46]\) and \( Z_2 \)-vortices (hedgehogs) as two types of topological defects. The hedgehog is stabilized by the orthogonality of the antiferromagnets. For instance, when one of them has fixed uniform orientation of its Néel order in space, the orthogonal orientation of the other one is free to make a hedgehog-like rotation.

Summary.— We have found surprising noncollinear spin order that arises from the NN spin-orbital superexchange when ferromagnetic and antiferromagnetic interactions almost compensate each other in the 2D KK model away from orbital degeneracy. It is stabilized by further neighbor spin exchange generated by entangled spin-orbital fluctuations which involve spin singlets and orbital flips. Similar mechanism works in the 3D KK model where it leads to a rich variety of spin-orbital phases to be reported elsewhere.

Finally, we note that magnetic order in spin-orbital systems may be changed by applying pressure \([47]\) —
Indeed a transition from ferromagnetic to antiferromagnetic order was observed in K$_2$CuF$_4$ [33,34]. Such a transition is also found here for a realistic value of $\eta \simeq 0.15$, and one could induce it in the antiferromagnetic phase by external magnetic field. Whether the antiferromagnetic order could be noncollinear as predicted here remains an experimental challenge.

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[1] K.I. Kugel and D.I. Khomskii, Sov. Phys. JETP 37, 725 (1973); Sov. Phys. Usp. 25, 231 (1982).
[2] B. Lake, D.A. Tennant, and S.E. Nagler, Phys. Rev. B 71, 134442 (2005); B. Lake, D.A. Tennant, C.D. Frost, and S.E. Nagler, Nature Materials 4, 329 (2005).
[3] Y. Tokura and N. Nagaosa, Science 288, 462 (2000).
[4] J.C. Wang, Y.Q. Li, and F.C. Zhang, Phys. Rev. B 80, 140401 (2009).
[5] G. Vidal, Phys. Rev. Lett. 92, 220405 (2004); ibid. 101, 110501 (2008); L. Cincio, J. Dziarmaga, and M.M. Rams, ibid. 100, 040603 (2008); see also Fig. 23 in: G. Evenbly and G. Vidal, Phys. Rev. B 79, 144108 (2009).
[6] W. Brzezicki and A.M. Oleś, Phys. Rev. B 83, 244408 (2011); Acta Phys. Polon. A 121, 1045 (2012) http://przyrwbm.icm.edu.pl/APP/ABSTR/121/a121-5-16.html
[7] This choice is motivated by a particular preference towards spin singlets with $|z\rangle$-like orbitals on the bonds.
[8] A.M. Oleś, L.F. Feiner, and J. Zaanen, Phys. Rev. B 61, 6257 (2000).
[9] M.V. Mostovoy and D.I. Khomskii, Phys. Rev. Lett. 92, 167201 (2004).
[10] In fact the orbitals are never fully polarized, e.g., considering finite Hund’s exchange $\eta = 0.05$ we get $t^x \simeq -0.496$ for $E_z = -2J$ in the left AF phase, $t^y \simeq 0.487$ for $E_z = 1J$ in the right AF phase and $t^z \simeq -0.466$ for $E_z = -0.5J$ in the PVB phase, where the deviations from $t^0 = -\frac{1}{3}$ are typically larger.
[11] M. Ishizuka, T. Yamada, K. Amaya, and S. Endo, J. Phys. Soc. Jpn. 65, 1927 (1996).
[12] M. Ishizuka et al., J. Magn. Magn. Mat. 177, 725 (1998); M. Ishizuka et al., Phys. Rev. B 57, 64 (1998).
[13] J. van den Brink, P. Horsch, F. Mack, and A.M. Oleś, Phys. Rev. B 59, 6795 (1999); W.-L. You, G.-S. Tian, and H.-Q. Lin, ibid. 75, 195118 (2007).
[14] L. Cincio, J. Dziarmaga, and A.M. Oleś, Phys. Rev. B 82, 104416 (2010).
[15] Due to this difference the ortho-AF phase exists in a more restricted range for $E_z > 0$: $\eta \simeq 0.29$ and $E_z > 3J$.
[16] Y. Akagi, M. Udagawa, and Y. Motome, Phys. Rev. Lett. 108, 096401 (2012).
[17] The spin interactions Eq. (3) exclude the spiral order.
[18] See supplemental material for more technical details.
[19] F. Wilczek and A. Zee, Phys. Rev. Lett. 51, 2250 (1983); D.A. Abanin, S.A. Parameswaran, and S.L. Sondhi, ibid. 103, 076802 (2009).
[20] Y. Ding et al., Phys. Rev. Lett. 102, 237201 (2009); J.-S. Zhou et al., Phys. Rev. B 80, 224422 (2009).
SUPPLEMENTAL MATERIAL

This supplement presents the technical details of the analysis employed in the paper. We first consider the third order terms in the perturbative expansion in section A. They justify the angle \( \varphi = \pi/2 \) obtained for the nearest neighbor (NN) spins in the regime of the non-collinear ortho-antiferromagnetic (ortho-AF) phase. In section B we develop the spin-wave theory for the ortho-AF phase and calculate the quantum corrections to the order parameter. These calculations show that the non-collinear ortho-AF phase is stable with respect to the Gaussian fluctuations and the quantum corrections are here weaker than for the two-dimensional (2D) AF Heisenberg model.

Third order terms in the perturbative expansion

The second order in the perturbation theory in \(|\varepsilon_z|^{-1}\) results in two antiferromagnets on interpenetrating sublattices, but the angle \( \varphi \) between the nearest neighbor (NN) spins remains undetermined, see Fig. 6(a). Thus we have to consider third order contributions to the effective spin Hamiltonian \( H_s \) of the form:

\[
H_s^{(3)} = \frac{1}{\varepsilon_z^2} \sum_{i,j,k} \sum_{\gamma} \left[-J^{xx}(\eta) S_i \cdot S_{i+\gamma} + K^{xx}(\eta)\right]
\]

\[\times \sum_{\gamma \neq \gamma'} \left[J^{xx}(\eta) S_i \cdot S_{i+\gamma + \gamma''} + K^{zz}(\eta)\right] \]

\[\times \sum_{\gamma' \neq \gamma'' \neq \gamma} \left[J^{xx}(\eta) S_i \cdot S_{i+\gamma + \gamma''} + K^{xx}(\eta)\right]
\]

\[\times \sum_{\gamma'' \neq \gamma'' \neq \gamma} \left[J^{xx}(\eta) S_i \cdot S_{i+\gamma + \gamma''} + K^{xx}(\eta)\right]
\]

where: \( J^{xx}(\eta) = 2^{-3} \sqrt{3} (r_1 + 2r_2 + 3r_4) \), \( K^{xx}(\eta) = 2^{-7} \sqrt{3} (2r_2 - 3r_1 + 3r_4) \), \( J^{xx}(\eta) = 2^{-5} (r_1 + r_4) \), and \( K^{xx}(\eta) = 2^{-7} (3r_1 - r_4) \). Here and in all other equations in this Section a sum over \( \gamma \) means the sum over all directions in the square lattice, i.e., \( \gamma = \pm a, \pm b \).

The spin chains with less than three scalar products do not contribute with any qualitatively new terms. Once they are omitted we obtain:

\[
H_s^{(3)} = \frac{9}{216 \varepsilon_z^2} \sum_{i,j,k} \sum_{\gamma} \sum_{\gamma' \neq \gamma} 
\left\{ 2s_\gamma s_{\gamma'} (S_{i+\gamma} \cdot S_i) (S_i \cdot S_{i+\gamma}) (S_{i+\gamma} \cdot S_{i+\gamma'}) + s_\gamma s_{\gamma'} (S_{i+\gamma} \cdot S_{i+\gamma'}) (S_{i+\gamma} \cdot S_{i+\gamma'}) \right\}
\]

Figure 6. Panel (a): two independent AF orders realized by effective spin Hamiltonian \( H_s \) up to second order. Angle \( \varphi \) between the two neighboring spins is undetermined. Panel (b): exemplary third order correction to \( H_s \) fixing the angle \( \varphi \) as \( \varphi = \pi/2 \). Red frames stand for Heisenberg bond with \( \pm \) sign depending on the bond's direction and magenta dots indicate the single-site orbital excitations in the ground state.

where \( s_\gamma \) is a sign factor depending on bond’s direction \( \gamma \) originating from the definition of operators \( \tau_i^{\mu,\nu} \) [see Fig. 6(b)], i.e.,

\[
s_\gamma = \begin{cases} 1 & \text{if } \gamma = \pm a \\ -1 & \text{if } \gamma = \pm b \end{cases}
\]

We transform the second term of Eq. (14) using the vector identity:

\[
(S_i \cdot S_{i+\gamma}) (S_i \cdot S_{i+\gamma'}) = (S_{i+\gamma'} \cdot S_i) (S_i \cdot S_{i+\gamma} + i S_{i+\gamma} \times S_i)
\]

The antihermitian term with a cross product cancels out under the sum in Eq. (13), thus we obtain:

\[
H_{\text{chain}}^{(3)} = \frac{9}{216 \varepsilon_z^2} \sum_{i,j,k} \sum_{\gamma} \sum_{\gamma' \neq \gamma} 
\left\{ 2s_\gamma s_{\gamma'} (S_{i+\gamma} \cdot S_i) (S_i \cdot S_{i+\gamma}) (S_{i+\gamma} \cdot S_{i+\gamma'}) + s_\gamma s_{\gamma'} (S_{i+\gamma} \cdot S_i) (S_i \cdot S_{i+\gamma}) (S_{i+\gamma} \cdot S_{i+\gamma'}) \right\}
\]

Now all the scalar products are ordered along the lines: \((i + \gamma) \rightarrow (i) \rightarrow (i + \gamma') \rightarrow (i + \gamma' + \gamma'')\) and \((i + \gamma') \rightarrow (i) \rightarrow (i + \gamma) \rightarrow (i + \gamma + \gamma'')\). Next we use another spin identity, namely

\[
(S_1 \cdot S_2) (S_2 \cdot S_3) (S_3 \cdot S_4) = \frac{1}{16} (S_1 \cdot S_4) + \frac{1}{4} (S_1 \cdot S_4) (S_2 \cdot S_3) - \frac{1}{4} (S_1 \cdot S_3) (S_2 \cdot S_4) + \frac{i}{8} (S_1 \cdot S_3 \times S_4) + \frac{i}{8} (S_1 \cdot S_4 \times S_2).
\]

Again, the antihermitian cross-product terms cancel out under the sums in \( H_{\text{chain}}^{(3)} \).

To analyze the relevance of other terms in Eq. (18) we have to take into account that, to second order in the perturbation theory, there is nearly classical AF order on
the two sublattices. We observe that:

(i) the first term is an AF interaction between the sublattices which is not compatible with the antiferromagnetism on the sublattices that is O(E) stronger,

(ii) depending on its sign the second term may favour orthogonality of the two AF orders which is compatible with the order on sublattices, and

(iii) the third term brings no new information about the order.

Taking into account all three above arguments we argue that the relevant type-(ii) third order perturbative contributions of the form given by Eq. (13) may favour orthogonality of the two AF orders. Now we have to extract all such contributions from Eq. (13) and check if their overall sign is indeed positive.

After transforming Eq. (17) we obtain

\[
H^{(3)}_\perp = \frac{9}{218 \varepsilon_\perp^2} (r_1 + r_4) (r_1 + 2r_2 + 4r_4)^2 \sum_{i,\gamma} \sum_{\gamma',\gamma''} \left[ 2 s_i s_{\gamma'} (S_{i+\gamma} \cdot S_{i+\gamma'+\gamma''}) (S_i \cdot S_{i+\gamma}) + s_i s_{\gamma''} (S_{i+\gamma'} \cdot S_{i+\gamma+\gamma''}) (S_i \cdot S_{i+\gamma}) \right],
\]

or in a more compact form

\[
H^{(3)}_\perp = \frac{27}{218 \varepsilon_\perp^2} (r_1 + r_4) (r_1 + 2r_2 + 4r_4)^2 \sum_{i,\gamma} (S_i, S_{i+\gamma}) \times \left( \sum_{\gamma' \neq \gamma} s_{\gamma'} (S_{i+\gamma'} \cdot (S_i, S_{i+\gamma+\gamma''})). \right)
\]

For two interpenetrating classical antiferromagnets \( H^{(3)}_\perp \) gives the energy per site,

\[
\varepsilon^{(3)}_\perp \approx \frac{1}{\varepsilon_\perp^2} \langle \langle \eta \rangle \rangle \xi(\eta) \left( \frac{3}{4} \cos \varphi \right)^2.
\]

This classical energy is minimized for \( \varphi = \pi/2 \), i.e., when the NN spins on the bonds are orthogonal. This completes the argument that the orders in the two antiferromagnets prefer to be orthogonal.

**Spin wave expansion in the noncollinear ortho-AF phase**

We start from the general form of the effective spin Hamiltonian:

\[
H_s = A \sum_{(ij)} S_i \cdot S_j + 2B \sum_{(\langle i|j \rangle)} S_i \cdot S_j - B \sum_{(\langle i|j \rangle)} S_i \cdot S_j + C \sum_{(ij)\langle \gamma|\gamma' \rangle} (S_i \cdot S_j) \sum_{\gamma' \neq \gamma} s_i s_{\gamma'} \theta (S_{i+\gamma'} \cdot S_{i+\gamma+\gamma''}),
\]

with coefficients \( A, B \) and \( C \) being the functions of \( \eta \) and \( \varepsilon_\perp \), i.e.,

\[
A = \frac{1}{25} (-3r_1 + 4r_2 + r_4) + \frac{1}{\varepsilon_\perp^2} \sum_{211} \left( 3 \left(r_1^2 - r_2^2\right) - 2 \left(r_1 + 2r_2 + 3r_4\right)^2 \right),
\]

\[
B = -\frac{1}{\varepsilon_\perp^2} \sum_{211} (r_1 + 2r_2 + 3r_4)^2,
\]

\[
C = \frac{27}{218 \varepsilon_\perp^2} (r_1 + r_4) (r_1 + 2r_2 + 3r_4)^2.
\]

To describe the ortho-AF order we divide the lattice into four sublattices as follows

\[
S^p_{i,j} = S_{p+2i,q+2j}, \quad p, q \in \{1, 2\},
\]

where \( p \) and \( q \) form the sublattice label. In what follows all the sums over \( p \) and \( q \) run over the set \{1, 2\}. Now, in each sublattice we do the linearized Holstein-Primakoff transformation around the ortho-AF order, i.e.,

\[
S_{i,j}^{x,11} = \frac{1}{2} \left( a_{i,j}^{11\dagger} + a_{i,j}^{11} \right), \quad S_{i,j}^{x,22} = \frac{1}{2} \left( a_{i,j}^{22\dagger} + a_{i,j}^{22} \right),
\]

\[
S_{i,j}^{x,12} = \frac{1}{2} \left( a_{i,j}^{12\dagger} - a_{i,j}^{12} \right), \quad S_{i,j}^{x,21} = \frac{1}{2} \left( a_{i,j}^{21\dagger} + a_{i,j}^{21} \right),
\]

\[
S_{i,j}^{z,11} = \frac{1}{2} \left( a_{i,j}^{11\dagger} + a_{i,j}^{11} \right), \quad S_{i,j}^{z,22} = \frac{1}{2} \left( a_{i,j}^{22\dagger} - a_{i,j}^{22} \right). \]

Next step is the Fourier transform (FT):

\[
a_{k,j}^{p,q} = \sum_{k} \epsilon^{-i(k_b j + k_a p)} a_{k,j}^{p,q},
\]

followed by the phase transformation, in order to get rid of imaginary parts in \( H_s \) of Eq. (22) after FT,

\[
a_{k,j}^{11\dagger} \rightarrow a_{k,j}^{11\dagger} e^{-i\frac{\pi}{4}}, \quad a_{k,j}^{12\dagger} \rightarrow ia_{k,j}^{12\dagger},
\]

\[
a_{k,j}^{21\dagger} \rightarrow -ia_{k,j}^{21\dagger} e^{-i\frac{\pi}{4}}, \quad a_{k,j}^{22\dagger} \rightarrow a_{k,j}^{22\dagger} e^{i\frac{\pi}{4}}.
\]

Finally, the interactions in the \( H_s \) Hamiltonian take the following form:

\[
\sum_{(ij)} S_i \cdot S_j = \frac{1}{2} \sum_{k} \left( a_{k,j}^{21\dagger} a_{k,j}^{21} \right) \left( a_{k,j}^{11\dagger} a_{k,j}^{11} \right) + \frac{1}{2} \sum_{k} \left( a_{k,j}^{12\dagger} a_{k,j}^{12} \right) \left( a_{k,j}^{22\dagger} a_{k,j}^{22} \right)
\]

\[
- \frac{1}{2} \sum_{k} \left( a_{k,j}^{12\dagger} a_{k,j}^{12} \right) \left( a_{k,j}^{11\dagger} a_{k,j}^{11} \right) + \frac{1}{2} \sum_{k} \left( a_{k,j}^{21\dagger} a_{k,j}^{21} \right) \left( a_{k,j}^{22\dagger} a_{k,j}^{22} \right),
\]

(31)
for the NN interactions,
\[ \sum_{\langle \langle i,j \rangle \rangle} \langle s_i, s_j \rangle = 2 \sum_{k} \gamma_k \left( a_{k}^{\dagger} + a_{-k}^{\dagger} \right) \left( a_{k} + a_{-k} \right) \]
for the NNN interactions,
\[ \sum_{\langle \langle \langle i,j \rangle \rangle \rangle} \langle s_i, s_j \rangle = 2 \sum_{k} \sum_{p,q} a_{k}^{pq} \rho_{k} \left( \gamma_k - 1 \right) \]
for the third order interactions between the two AF sublattices. The coefficients \( \langle \gamma_k, \gamma_k' \rangle \) are defined as:
\[ \gamma_k = \frac{1}{2} \left( \cos k_b + \cos k_a \right), \]
\[ \gamma_k' = \frac{1}{2} \left( \cos \frac{k_a + k_b}{2} + \cos \frac{k_a - k_b}{2} \right). \]

The last step is the Bogoliubov transformation of the block-diagonal Hamiltonian \( H_s \) in the momentum space. The most general form of this transformation is:
\[ \begin{pmatrix} b_{k}^{\dagger} \\ b_{-k} \end{pmatrix} = B_k \begin{pmatrix} a_{k}^{\dagger} \\ a_{-k} \end{pmatrix}, \]
Here \( b_{k} \) are the new boson operators and \( B_k \) is an \( 8 \times 8 \) transformation matrix to be determined from the Bogoliubov-de Gennes eigenequation,
\[ [H_s, b_{k}^{pq \dagger}] = E_{k}^{pq} b_{k}^{pq \dagger}, \]
equivalent to an \( 8 \times 8 \) matrix eigenproblem with hyperbolic normalization conditions typical for bosons. The resulting eigen-vectors form the rows \( B_k \) and the excitation energies \( E_{k}^{pq} \) can be expressed analytically as,
\[ (E_{k}^{pq})^2 = 2^{4} \left( 1 - \gamma_k^{pq} \right) \left\{ B - 6C + (B - 24C) \gamma_k^{pq} \right\} \times \left\{ 3B + A \gamma_k^{pq} - B \left( \gamma_k - 2 \right) \right\}, \]
with
\[ \gamma_k^{pq} = \frac{1}{2} \left\{ \left( -1 \right)^p \cos \frac{k_a}{2} + \left( -1 \right)^q \cos \frac{k_b}{2} \right\}. \]
As might have been expected, in addition to the three gapless Goldstone modes for \( (p, q) = (2, 2), (1, 2), (2, 1) \), there is one gapped branch \( E_{k=0}^{11} \), with \( E_{k=0}^{11} = 24\sqrt{4B - A}C \), related to the rigidity of the angle \( \varphi \) between the two antiferromagnets.

Another important quantity is the magnetization on a sublattice which quantifies quantum fluctuations. For instance, the ground state expectation value of \( S_{i, j}^{z, 11} \) can be expressed by the elements of \( B_k \),
\[ \left\langle S_{i, j}^{z, 11} \right\rangle = \frac{1}{2} - \frac{1}{4\pi^2} \int_{-\pi}^{\pi} \sum_{p=5}^{8} \left( B_k^{-1} \right)^2 \rho^2 k. \]
The integrand in the above formula can be obtained analytically whereas the integration is non-algebraic. In Figs. 7 and 8 we show the behavior of \( \left\langle S_{i, j}^{z, 11} \right\rangle \) along different cuts of the ortho-AF phase.
Figure 8. The sublattice magnetization $\langle S^{z,11}_{i,j} \rangle$ as function of $\eta$ in the ortho-AF phase for $\varepsilon_z = -10$ (solid line). Dashed line marks the value of $\eta_0$ where $A = 0$. The vertical solid (red) lines are boundaries of the spin-wave expansion, where the integral (41) becomes divergent.

Both cuts in Fig. 7 take the same value of $\langle S^{z,11}_{i,j} \rangle \simeq 0.385$ in the limit of $\varepsilon_z \to -\infty$ when the coupling between the two antiferromagnets is negligible. This magnetization is markedly higher than that for the 2D AF Heisenberg model, where $\langle S^z \rangle \simeq 0.303$. This confirms that the NNN FM interactions in $H_s$ make the AF order more robust against quantum fluctuations. What is more, along the line $\eta_0(\varepsilon_z)$ (blue curve) the third order term $\propto C$ enhances the order parameter up to $\langle S^{z,11}_{i,j} \rangle \simeq 0.405$ near $\varepsilon_z = -4$. Deviations from the path $\eta_0(\varepsilon_z)$ that introduce nonzero coefficient $A$ of the NN AF coupling can either impair or enhance the ortho-AF order. For instance, the red curve lies below the blue one in Fig. 7. In contrast, the cut along the line $\varepsilon_z = -10$ in Fig. 8 shows that a small increase of $\eta$ above $\eta_0$ can increase the magnetization (at this value of $\varepsilon_z$). This reflects the proximity to the ferromagnetic phase where the quantum fluctuations reducing the order parameter $\langle S^{z,11}_{i,j} \rangle$ are suppressed.

The sudden collapse of the blue and red curves in Fig. 7 terminates the ortho-AF phase in the spin wave approach. However, this is not a definitive conclusion because the perturbative Hamiltonian $H_s$ underlying the spin wave expansion is not self-consistent for $\varepsilon_z > -4$, where the third order term $\propto C$ in $H_s$ dominates over the second order term $\propto B$. In the non-perturbative plaquette MF the ortho-AF phase extends far beyond the perturbative regime, and it is even more extended in the more accurate ERA approach.