Supplementary Material: Basic Aspects of Ferroelectricity Induced by Noncollinear Alignment of Spins

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A. General form of magneto-electric coupling in centrosymmetric bond

Consider two sites, 1 and 2, which are connected by the spatial inversion (Figure S1). The corresponding inversion center is located in the mid-point of the bond, connecting these two sites. Our goal here is to find a phenomenological expression for the electric polarization, induced by the noncollinear arrangement of spins. Let $\boldsymbol{e}_1 = (e_1^x, e_1^y, e_1^z)$ and $\boldsymbol{e}_2 = (e_2^x, e_2^y, e_2^z)$ be the directions of spins at the sites 1 and 2, whose lengths are normalized to 1: $|\boldsymbol{e}_1|^2 = |\boldsymbol{e}_2|^2 = 1$. Then, very generally, one can define the ferromagnetic ($\boldsymbol{F}$) and antiferromagnetic ($\boldsymbol{A}$) order parameters as

$$\boldsymbol{F} = \boldsymbol{e}_1 + \boldsymbol{e}_2 \tag{1}$$

$$\boldsymbol{A} = \boldsymbol{e}_1 - \boldsymbol{e}_2. \tag{2}$$

Therefore, the spatial inversion ($\mathcal{I}$) transforms $\boldsymbol{F}$ to $\boldsymbol{F}$ and $\boldsymbol{A}$ to $-\boldsymbol{A}$. The time reversal ($\mathcal{T}$) changes the sign of both $\boldsymbol{F}$ and $\boldsymbol{A}$. Then, $\mathcal{IT}$ will transform $\boldsymbol{F}$ to $-\boldsymbol{F}$ and $\boldsymbol{A}$ to $\boldsymbol{A}$. If noncollinear magnetic arrangement obeys certain symmetry rules, both $\boldsymbol{F}$ and $\boldsymbol{A}$ should be invariant under this symmetry operation. However, in the case of $\boldsymbol{F}$ this operation is $\mathcal{I}$, but in the case of $\boldsymbol{A}$ it is $\mathcal{IT}$. Thus, if $\boldsymbol{A} = 0$ or $\boldsymbol{F} = 0$, the inversion symmetry is preserved (either as it is or in the combination with $\mathcal{T}$) and there will be no electric polarization. However, both $\boldsymbol{F}$ and $\boldsymbol{A}$ are finite, the inversion symmetry is inevitably broken by the magnetic order, as there is no symmetry operation, which would simultaneously transform $\boldsymbol{F}$ to $\boldsymbol{F}$ and $\boldsymbol{A}$ to $\boldsymbol{A}$.

Thus, from the phenomenological point of view, the polarization $\vec{P}$ should be proportional to both $\boldsymbol{F}$ and $\boldsymbol{A}$ and vanish if either of them vanishes. The most general construction of this type is the Kronecker product $\hat{W} = \boldsymbol{F}^T \otimes \boldsymbol{A}$, where $\boldsymbol{F}^T$ is the row-vector, corresponding to the column-vector $\boldsymbol{F}$. Using Eqs. (1)-(2), one gets:

$$\hat{W} = \begin{pmatrix} (e_1^x)^2 - (e_2^x)^2 & (e_1^x + e_2^x)(e_1^y - e_2^y) & (e_1^x + e_2^x)(e_1^z - e_2^z) \\ (e_1^y + e_2^y)(e_1^x - e_2^x) & (e_1^y)^2 - (e_2^y)^2 & (e_1^y + e_2^y)(e_1^z - e_2^z) \\ (e_1^z + e_2^z)(e_1^x - e_2^x) & (e_1^z + e_2^z)(e_1^y - e_2^y) & (e_1^z)^2 - (e_2^z)^2 \end{pmatrix}. \tag{3}$$

First, we note that $\mathrm{Tr}\hat{W} = 0$. Then, $\hat{W}$ can be identically rearranged in terms of its symmetric (S) and antisymmetric (A) parts: $\hat{W} = \hat{W}^{(S)} + \hat{W}^{(A)}$, where

$$\hat{W}^{(S)} = \frac{1}{2}(\hat{W} + \hat{W}^T) = \begin{pmatrix} e_1^x e_1^x - e_2^x e_2^x & e_1^x e_1^y - e_2^x e_2^y & e_1^x e_1^z - e_2^x e_2^z \\ e_1^y e_1^x - e_2^y e_2^x & e_1^y e_1^y - e_2^y e_2^y & e_1^y e_1^z - e_2^y e_2^z \\ e_1^z e_1^x - e_2^z e_2^x & e_1^z e_1^y - e_2^z e_2^y & e_1^z e_1^z - e_2^z e_2^z \end{pmatrix} \tag{4}$$

and

$$\hat{W}^{(A)} = \frac{1}{2}(\hat{W} - \hat{W}^T) = \begin{pmatrix} 0 & -[\boldsymbol{e}_1 \times \boldsymbol{e}_2]^z & [\boldsymbol{e}_1 \times \boldsymbol{e}_2]^y \\ [\boldsymbol{e}_1 \times \boldsymbol{e}_2]^z & 0 & -[\boldsymbol{e}_1 \times \boldsymbol{e}_2]^x \\ -[\boldsymbol{e}_1 \times \boldsymbol{e}_2]^y & [\boldsymbol{e}_1 \times \boldsymbol{e}_2]^x & 0 \end{pmatrix}. \tag{5}$$

Since $\vec{P} \sim \hat{W}$, we should have:

$$\vec{P} = \vec{\boldsymbol{\mathcal{P}}}_{12} \cdot [\boldsymbol{e}_1 \times \boldsymbol{e}_2] + \boldsymbol{e}_1 \cdot \vec{\Pi} \boldsymbol{e}_1 - \boldsymbol{e}_2 \cdot \vec{\Pi} \boldsymbol{e}_2. \tag{6}$$

Thus, there can be only two sources of polarization in the centrosymmetric bonds. The first one, given by the 1st term in Eq. (6), is due to inverse Dzyaloshinskii-Moriya mechanism [1]. The second one, given by the 2nd and 3rd terms, is the difference of single-ion contributions stemming from the noncollinear alignment of spins.

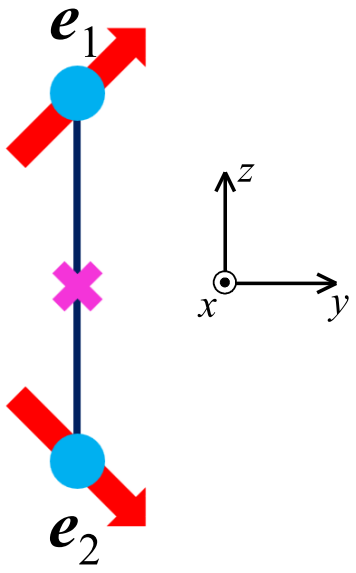


Figure S1. Cartoon picture explaining the geometry of centrosymmetric bond and noncollinear arrangement of spins in this bond. The inversion center is denoted by $\times$. $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$ are the directions of spins at two sites of the bonds.

B. General form of position operator in the basis of Kramers states

Without the loss of generality, two states of the Kramers doublet can be taken in the following form:

$$|+\rangle = |\psi^0 \uparrow\rangle + |\Delta\psi \downarrow\rangle \tag{7}$$
$$|-\rangle = |\psi^0 \downarrow\rangle - |\Delta\psi^* \uparrow\rangle, \tag{8}$$

where the symbols $\uparrow$ and $\downarrow$ explicitly stand for the spin part, while ψ^0 and $\Delta\psi$ describe the coordinate part. ψ^0 can be viewed as the main component, which exists even without spin-orbit (SO) interaction, while $\Delta\psi$ is induced solely by the SO coupling. Furthermore, by appropriately choosing the phases, ψ^0 can be taken as real, while $\Delta\psi$ can be complex. If $\mathcal{T} = i\hat{\sigma}^y\hat{K}$ is the time-reversal operator (where $\hat{\sigma}^y$ is the Pauli matrix and K stands for the complex conjugation), it holds $\mathcal{T}|+\rangle = -|-\rangle$ and $\mathcal{T}|-\rangle = |+\rangle$. $|+\rangle$ and $|-\rangle$ are supposed to be normalized $\langle+|+\rangle = \langle-|-\rangle = 1$. The typical examples are the $j = 1/2$ (Γ_7) states [1],

$$|+\rangle = \frac{1}{\sqrt{3}}\left(|xy \uparrow\rangle + |yz \downarrow\rangle + i|zx \downarrow\rangle\right) \tag{9}$$
$$|-\rangle = \frac{1}{\sqrt{3}}\left(|xy \downarrow\rangle - |yz \uparrow\rangle + i|zx \uparrow\rangle\right), \tag{10}$$

or the z^2 states [2]

$$|+\rangle = \frac{1}{\sqrt{1+2\xi^2}}\left(|z^2 \uparrow\rangle + i\xi|yz \downarrow\rangle + \xi|zx \downarrow\rangle\right) \tag{11}$$
$$|-\rangle = \frac{1}{\sqrt{1+2\xi^2}}\left(|z^2 \downarrow\rangle + i\xi|yz \uparrow\rangle - \xi|zx \uparrow\rangle\right). \tag{12}$$

Eqs. (7) and (8) can be identically rewritten as

$$|+\rangle = |\psi^0 \uparrow\rangle + |\mathrm{Re}\Delta\psi \downarrow\rangle + i|\mathrm{Im}\Delta\psi \downarrow\rangle \tag{13}$$
$$|-\rangle = |\psi^0 \downarrow\rangle - |\mathrm{Re}\Delta\psi \uparrow\rangle + i|\mathrm{Im}\Delta\psi \uparrow\rangle. \tag{14}$$

Then, we our goal is to calculate matrix elements of the position operator,

$$\hat{\vec{r}}_{ij} = \begin{pmatrix} \langle i+|\vec{r}|j+\rangle & \langle i+|\vec{r}|j-\rangle \\ \langle i-|\vec{r}|j+\rangle & \langle i-|\vec{r}|j-\rangle \end{pmatrix}, \tag{15}$$

in the basis of Kramers states at the sites i and j. This $\hat{\vec{r}}_{ij}$ can be decomposed in terms of unity $\hat{\mathbb{1}}$ and the vector $\hat{\boldsymbol{\sigma}} = (\hat{\sigma}^x, \hat{\sigma}^y, \hat{\sigma}^z)$ of Pauli matrices as $\hat{\vec{r}}_{ij} = \vec{r}^0_{ij}\hat{\mathbb{1}} + i\vec{\boldsymbol{r}}_{ij}\hat{\boldsymbol{\sigma}}$. The, using Eqs. (13) and (14), one can find:

$$\begin{aligned}
\langle i+|\vec{r}|j+\rangle &= \langle\psi^0_i|\vec{r}|\psi^0_j\rangle + \langle \mathrm{Re}\Delta\psi_i|\vec{r}|\mathrm{Re}\Delta\psi_j\rangle + \langle \mathrm{Im}\Delta\psi_i|\vec{r}|\mathrm{Im}\Delta\psi_j\rangle + i\langle \mathrm{Re}\Delta\psi_i|\vec{r}|\mathrm{Im}\Delta\psi_j\rangle - i\langle \mathrm{Im}\Delta\psi_i|\vec{r}|\mathrm{Re}\Delta\psi_j\rangle\\
\langle i+|\vec{r}|j-\rangle &= -\langle\psi^0_i|\vec{r}|\mathrm{Re}\Delta\psi_j\rangle + \langle \mathrm{Re}\Delta\psi_i|\vec{r}|\psi^0_j\rangle + i\langle\psi^0_i|\vec{r}|\mathrm{Im}\Delta\psi_j\rangle - i\langle \mathrm{Im}\Delta\psi_i|\vec{r}|\psi^0_j\rangle\\
\langle i-|\vec{r}|j+\rangle &= \langle\psi^0_i|\vec{r}|\mathrm{Re}\Delta\psi_j\rangle - \langle \mathrm{Re}\Delta\psi_i|\vec{r}|\psi^0_j\rangle + i\langle\psi^0_i|\vec{r}|\mathrm{Im}\Delta\psi_j\rangle - i\langle \mathrm{Im}\Delta\psi_i|\vec{r}|\psi^0_j\rangle\\
\langle i-|\vec{r}|j-\rangle &= \langle\psi^0_i|\vec{r}|\psi^0_j\rangle + \langle \mathrm{Re}\Delta\psi_i|\vec{r}|\mathrm{Re}\Delta\psi_j\rangle + \langle \mathrm{Im}\Delta\psi_i|\vec{r}|\mathrm{Im}\Delta\psi_j\rangle - i\langle \mathrm{Re}\Delta\psi_i|\vec{r}|\mathrm{Im}\Delta\psi_j\rangle + i\langle \mathrm{Im}\Delta\psi_i|\vec{r}|\mathrm{Re}\Delta\psi_j\rangle
\end{aligned}$$

Then, it is straightforward to obtain the following expressions for $\vec{r}^0_{ij}$ and $\vec{\boldsymbol{r}}_{ij} = (\vec{r}^x_{ij}, \vec{r}^y_{ij}, \vec{r}^z_{ij})$:

$$\vec{r}^0_{ij} = \langle\psi^0_i|\vec{r}|\psi^0_j\rangle + \langle \mathrm{Re}\Delta\psi_i|\vec{r}|\mathrm{Re}\Delta\psi_j\rangle + \langle \mathrm{Im}\Delta\psi_i|\vec{r}|\mathrm{Im}\Delta\psi_j\rangle \tag{16}$$

$$\vec{r}^x_{ij} = \langle\psi^0_i|\vec{r}|\mathrm{Im}\Delta\psi_j\rangle - \langle \mathrm{Im}\Delta\psi_i|\vec{r}|\psi^0_j\rangle \tag{17}$$

$$\vec{r}^y_{ij} = -\langle\psi^0_i|\vec{r}|\mathrm{Re}\Delta\psi_j\rangle + \langle \mathrm{Re}\Delta\psi_i|\vec{r}|\psi^0_j\rangle \tag{18}$$

$$\vec{r}^z_{ij} = \langle \mathrm{Re}\Delta\psi_i|\vec{r}|\mathrm{Im}\Delta\psi_j\rangle - \langle \mathrm{Im}\Delta\psi_i|\vec{r}|\mathrm{Re}\Delta\psi_j\rangle. \tag{19}$$

Thus, $\vec{r}^0_{ij}$ is symmetric with respect to the permutation of i and j: $\vec{r}^0_{ji} = \vec{r}^0_{ij}$, while $\vec{\boldsymbol{r}}_{ij}$ is antisymmetric: $\vec{\boldsymbol{r}}_{ji} = -\vec{\boldsymbol{r}}_{ij}$.

C. Symmetry properties of $\vec{\boldsymbol{r}}_{ij}$: the groups C_2 and C_4

In this section, we consider the symmetry properties of $\vec{\boldsymbol{r}}_{ij}$ under the fourfold rotations about z. Thus, there are four symmetry operations in the group: the 90°, 180°, and 270° rotations about z (respectively, $\hat{R}^1$, $\hat{R}^2$, and $\hat{R}^3$), together with the unity $\hat{R}^0 = \hat{E}$. Then, each $\hat{R}^n$ combines the rotations in the spin (S) and orbital (L) subspace: $\hat{R}^n = \hat{R}^n_L\hat{R}^n_S$, obeying certain rules, as specified in Table I.

Table S1. Transformations of (x, y, z), and $(\mathrm{Re}\Delta\psi, \mathrm{Im}\Delta\psi)$ under the fourfold rotations $\hat{R}^n$ about z, and the spin matrices $\hat{R}^n_S$, corresponding to these rotations.

rotation	$\hat{R}^n_L(x,y,z)$	$\hat{R}^n_L(\mathrm{Re}\Delta\psi, \mathrm{Im}\Delta\psi)$	$\hat{R}^n_S$
$\hat{R}^1$	$(-y, x, z)$	$(\mp\mathrm{Im}\Delta\psi, \pm\mathrm{Re}\Delta\psi)$	$\begin{pmatrix} e^{i\frac{\pi}{4}} & 0 \\ 0 & e^{-i\frac{\pi}{4}} \end{pmatrix}$
$\hat{R}^2$	$(-x, -y, z)$	$(-\mathrm{Re}\Delta\psi, -\mathrm{Im}\Delta\psi)$	$\begin{pmatrix} e^{i\frac{\pi}{2}} & 0 \\ 0 & e^{-i\frac{\pi}{2}} \end{pmatrix}$
$\hat{R}^3$	$(y, -x, z)$	$(\pm\mathrm{Im}\Delta\psi, \mp\mathrm{Re}\Delta\psi)$	$\begin{pmatrix} e^{i\frac{3\pi}{4}} & 0 \\ 0 & e^{-i\frac{3\pi}{4}} \end{pmatrix}$

Then, using explicit form of $\hat{R}^1_S$, one can find:

$$\hat{R}^1|+\rangle = e^{i\frac{\pi}{4}}\hat{R}^1_L\left(|\psi^0\uparrow\rangle - i|\Delta\psi\downarrow\rangle\right) \tag{20}$$

$$\hat{R}^1|-\rangle = e^{-i\frac{\pi}{4}}\hat{R}^1_L\left(|\psi^0\downarrow\rangle - i|\Delta\psi^*\uparrow\rangle\right). \tag{21}$$

Moreover, it holds $\hat{R}^1_L|\psi^0\rangle = \pm|\psi^0\rangle$, as it should take place without SO coupling. The sign depends on whether $|\psi^0\rangle$ forms an even or odd representation of the group for the bond ij (for instance, it is $-$ for the $j = 1/2$ states and $+$ for the z^2 states). Then, the requirement that $\hat{R}^1|+\rangle$ should coincide with $|+\rangle$ apart from the phase, leads to the following symmetry properties for the coordinate part:

$$\hat{R}^1_L|\mathrm{Re}\Delta\psi\rangle = \mp|\mathrm{Im}\Delta\psi\rangle \tag{22}$$

$$\hat{R}^1_L|\mathrm{Im}\Delta\psi\rangle = \pm|\mathrm{Re}\Delta\psi\rangle. \tag{23}$$

Considering the same argument for $\hat{R}^2$, one can get:

$$\hat{R}^2|+\rangle = e^{i\frac{\pi}{2}}\hat{R}^2_L\left(|\psi^0\uparrow\rangle - |\Delta\psi\downarrow\rangle\right) \tag{24}$$

$$\hat{R}^2|-\rangle = e^{-i\frac{\pi}{2}}\hat{R}^2_L\left(|\psi^0\downarrow\rangle + |\Delta\psi^*\uparrow\rangle\right) \tag{25}$$

and

$$\hat{R}_L^2|\mathrm{Re}\Delta\psi\rangle = -|\mathrm{Re}\Delta\psi\rangle \tag{26}$$
$$\hat{R}_L^2|\mathrm{Im}\Delta\psi\rangle = -|\mathrm{Im}\Delta\psi\rangle. \tag{27}$$

Finally, the consideration of $\hat{R}^3$ will yield

$$\hat{R}^3|+\rangle = e^{i\frac{3\pi}{4}}\hat{R}_L^3\left(|\psi^0\uparrow\rangle + i|\Delta\psi\downarrow\rangle\right) \tag{28}$$
$$\hat{R}^3|-\rangle = e^{-i\frac{3\pi}{4}}\hat{R}_L^3\left(|\psi^0\downarrow\rangle + i|\Delta\psi^*\uparrow\rangle\right) \tag{29}$$

and

$$\hat{R}_L^3|\mathrm{Re}\Delta\psi\rangle = \pm|\mathrm{Im}\Delta\psi\rangle \tag{30}$$
$$\hat{R}_L^3|\mathrm{Im}\Delta\psi\rangle = \mp|\mathrm{Re}\Delta\psi\rangle. \tag{31}$$

First, we consider the symmetry properties of $\vec{\boldsymbol{r}}_{ij}$ when there is only twofold rotation symmetry about z (the group C_2). Our goal is to find which elements of $\vec{\boldsymbol{r}}_{ij}$ will remain finite after the symmetrization

$$\vec{\boldsymbol{r}}_{ij} \to \frac{1}{2}\sum_{n=0,2}\hat{R}_L^n\vec{\boldsymbol{r}}_{ij}, \tag{32}$$

where $\hat{R}_L^n$ acts both on the coordinate part of the Kramers states and $\vec{r}$. Then, x and y change the sign under $\hat{R}_L^2$ (see Table I), while z does not. Furthermore, the combination of ψ^0 and either Re or Im parts of $\Delta\psi$ changes the sign, while any combination of the Re or Im parts of $\Delta\psi$ does not. Therefore, the tensor $\vec{\boldsymbol{r}}_{ij}$ should have the following form [3]:

$$\vec{\boldsymbol{r}}_{ij} = \begin{pmatrix} r_{ij}^{x,x} & r_{ij}^{x,y} & 0 \\ r_{ij}^{y,x} & r_{ij}^{y,y} & 0 \\ 0 & 0 & r_{ij}^{z,z} \end{pmatrix}. \tag{33}$$

Next, we consider the transformation of $\vec{\boldsymbol{r}}_{ij}$ under all four symmetry operation of the group C_4:

$$\vec{\boldsymbol{r}}_{ij} \to \frac{1}{4}\sum_{n=0}^{3}\hat{R}_L^n\vec{\boldsymbol{r}}_{ij}. \tag{34}$$

Then, it is straightforward to obtain that:

$$r_{ij}^{x,x} = \frac{1}{2}\left(\langle\psi_i^0|x|\mathrm{Im}\Delta\psi_j\rangle - \langle\mathrm{Im}\Delta\psi_i|x|\psi_j^0\rangle - \langle\psi_i^0|y|\mathrm{Re}\Delta\psi_j\rangle + \langle\mathrm{Re}\Delta\psi_i|y|\psi_j^0\rangle\right) \tag{35}$$
$$r_{ij}^{y,x} = \frac{1}{2}\left(\langle\psi_i^0|y|\mathrm{Im}\Delta\psi_j\rangle - \langle\mathrm{Im}\Delta\psi_i|y|\psi_j^0\rangle + \langle\psi_i^0|x|\mathrm{Re}\Delta\psi_j\rangle - \langle\mathrm{Re}\Delta\psi_i|x|\psi_j^0\rangle\right) \tag{36}$$
$$r_{ij}^{x,y} = \frac{1}{2}\left(-\langle\psi_i^0|x|\mathrm{Re}\Delta\psi_j\rangle + \langle\mathrm{Re}\Delta\psi_i|x|\psi_j^0\rangle - \langle\psi_i^0|y|\mathrm{Im}\Delta\psi_j\rangle + \langle\mathrm{Im}\Delta\psi_i|y|\psi_j^0\rangle\right) \tag{37}$$
$$r_{ij}^{y,y} = \frac{1}{2}\left(-\langle\psi_i^0|y|\mathrm{Re}\Delta\psi_j\rangle + \langle\mathrm{Re}\Delta\psi_i|y|\psi_j^0\rangle + \langle\psi_i^0|x|\mathrm{Im}\Delta\psi_j\rangle - \langle\mathrm{Im}\Delta\psi_i|x|\psi_j^0\rangle\right). \tag{38}$$

Therefore, in comparison with the group C_2, we will have two additional properties, $r_{ij}^{x,x} = r_{ij}^{y,y}$ and $r_{ij}^{y,x} = -r_{ij}^{x,y}$, and the tensor $\vec{\boldsymbol{r}}_{ij}$ will have the following form:

$$\vec{\boldsymbol{r}}_{ij} = \begin{pmatrix} r_{ij}^{x,x} & -r_{ij}^{y,x} & 0 \\ r_{ij}^{y,x} & r_{ij}^{x,x} & 0 \\ 0 & 0 & r_{ij}^{z,z} \end{pmatrix}. \tag{39}$$

Another set of properties can be derived by considering the explicit dependence of $\mathrm{Re}\Delta\psi$ and $\mathrm{Im}\Delta\psi$ on the azimuthal angle φ. Then, $x \sim \cos\varphi$ and $y \sim \sin\varphi$, so that the rotations by 90, 180, and 270 degrees, corresponding to the transformations $\varphi \to \varphi + \frac{\pi}{2}$, $\varphi \to \varphi + \pi$, and $\varphi \to \varphi + \frac{3\pi}{2}$, respectively, will change the coordinates x, y, and z, as explained in Table I. Then, for the even representation, we have $\hat{R}^1|\psi^0\rangle = |\psi^0\rangle$. Then, $\mathrm{Re}\Delta\psi$ and $\mathrm{Im}\Delta\psi$ transform as x and y, respectively (see Table I). All together, it seems reasonable to assume that $\mathrm{Re}\Delta\psi \sim \cos\varphi$, $\mathrm{Im}\Delta\psi \sim \sin\varphi$,

and ψ^0 does not depend on φ. For the odd representation, $\hat{R}^1|\psi^0\rangle = -|\psi^0\rangle$, $\mathrm{Im}\Delta\psi$ and $\mathrm{Re}\Delta\psi$ transform as x and y, respectively. In this case, it is reasonable to assume that $\mathrm{Im}\Delta\psi \sim \cos\varphi$, $\mathrm{Re}\Delta\psi \sim \sin\varphi$, and $\psi^0 \sim \sin 2\varphi$. Then, the integration over φ should lead to $r_{ij}^{x,x} = r_{ij}^{y,y} = r_{ij}^{z,z} = 0$ and

$$r_{ij}^{y,x} = \langle\psi_i^0|y|\mathrm{Im}\Delta\psi_j\rangle - \langle\mathrm{Im}\Delta\psi_i|y|\psi_j^0\rangle = \langle\psi_i^0|x|\mathrm{Re}\Delta\psi_j\rangle - \langle\mathrm{Re}\Delta\psi_i|x|\psi_j^0\rangle, \tag{40}$$

for both representations.

Thus, for the C_4 symmetry, the tensor $\vec{\boldsymbol{r}}_{ij}$ has the following form:

$$\vec{\boldsymbol{r}}_{ij} = \begin{pmatrix} 0 & -r_{ij}^{y,x} & 0 \\ r_{ij}^{y,x} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{41}$$

which leads to the well-known expression $\vec{P} \sim \boldsymbol{\epsilon}_{ij} \times [\boldsymbol{e}_i \times \boldsymbol{e}_j]$ [1].

It appears that the form of Eq. (41) depends on the order of Kramers states. The interchange $|+\rangle$ and $|-\rangle$ will change the sign of $\vec{r}_{ij}^{\,y}$ and $\vec{r}_{ij}^{\,z}$, but not the one of $\vec{r}_{ij}^{\,x}$: see Eqs. (17)-(19) and equations above them. This leads to the alternative (formally, symmetric) representation for $\vec{\boldsymbol{r}}_{ij}$ [2]:

$$\vec{\tilde{\boldsymbol{r}}}_{ij} = \begin{pmatrix} 0 & \tilde{r}_{ij}^{y,x} & 0 \\ \tilde{r}_{ij}^{y,x} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{42}$$

such that $\tilde{r}_{ij}^{y,x} = r_{ij}^{y,x}$, but $\tilde{r}_{ij}^{x,y} = -r_{ij}^{x,y} = r_{ij}^{y,x} = \tilde{r}_{ij}^{y,x}$. Such behavior is related to the properties of the pseudospin states. If $|\pm z\rangle \equiv |\pm\rangle$ are pseudospine states in the positive and negative directions of the z axis, corresponding to them pseudospin states in the positive and negative directions of the axes x and y are given by $|\pm x\rangle = \frac{1}{\sqrt{2}}|+\rangle \pm \frac{1}{\sqrt{2}}|-\rangle$ and $|\pm y\rangle = \pm\frac{1-i}{2}|+\rangle + \frac{1+i}{2}|-\rangle$ [4]. Then, it is straightforward to see that the interchange of $|+z\rangle$ and $|-z\rangle$ will also interchange the order of the $|+y\rangle$ and $|-y\rangle$ states (apart from a phase) but not the one of $|+x\rangle$ and $|-x\rangle$ states, which is directly related to the behavior of the tensor $\vec{\tilde{\boldsymbol{r}}}_{ij}$. From the viewpoint of the spin model, the representations with the direct and reversed order of the states $|+\rangle$ and $|-\rangle$ should equivalent. Basically, it is our choice what to call the "spin up" and "spin down" states. Nevertheless, one should be careful by considering the interaction of pseudospin with the physical magnetic field, which should not depend on the representation. Particularly, it is important to remember that the interaction, $-\mu_\mathrm{B}\,\boldsymbol{\mathcal{S}}_i \cdot \mathfrak{g}_i \boldsymbol{H}$, of the pseudospin $\boldsymbol{\mathcal{S}}_i$ ($\boldsymbol{\mathcal{S}}_i = \frac{1}{2}\boldsymbol{e}_i$ for the single Kramers doublet) with the external magnetic field $\boldsymbol{H}$ is mediated by the 3×3 g-tensor, which is given by the matrix elements of $\hat{\boldsymbol{\sigma}}$ and the angular momentum operator $\hat{\boldsymbol{L}} = (\hat{L}^x, \hat{L}^y, \hat{L}^z)$ in the basis of Kramers states and also depends on the order of these states [4]. Therefore, the definitions of the tensors $\vec{\boldsymbol{r}}_{ij}$ and $\mathfrak{g}_i$ should be consistent with each other and use the same order of the Kramers states.

Applying four symmetry operations of the group C_4 to $\mathrm{Re}\Delta\psi$ and $\mathrm{Im}\Delta\psi$, it is straightforward to find that these Re and Im parts are orthogonal: $\langle\mathrm{Re}\Delta\psi|\mathrm{Im}\Delta\psi\rangle = \langle\mathrm{Im}\Delta\psi|\mathrm{Re}\Delta\psi\rangle = 0$. However, this is not the case for the C_2 symmetry, where $\mathrm{Re}\Delta\psi$ and $\mathrm{Im}\Delta\psi$ are not necessary orthogonal each other.

D. Symmetry properties of $\vec{\boldsymbol{r}}_{ij}$: the group C_3

In this section, we consider the symmetry properties of $\vec{\boldsymbol{r}}_{ij}$ under the threefold rotations about z. Thus, there are three symmetry operations in the group: the 120°- and 240°-rotations about z (respectively, $\hat{R}^1$ and $\hat{R}^2$), together with the unity $\hat{R}^0 = \hat{E}$. The corresponding transformations of (x, y, z) and $\hat{R}_S^n$ are given in Table II.

Then, using explicit form of $\hat{R}_S^1$, one can find:

$$\hat{R}^1|+\rangle = e^{i\frac{\pi}{3}}\hat{R}_L^1\left(|\psi^0\uparrow\rangle + e^{-i\frac{2\pi}{3}}|\Delta\psi\downarrow\rangle\right) \tag{43}$$

$$\hat{R}^1|-\rangle = e^{-i\frac{\pi}{3}}\hat{R}_L^1\left(|\psi^0\downarrow\rangle - e^{i\frac{2\pi}{3}}|\Delta\psi^*\uparrow\rangle\right), \tag{44}$$

which should lead to the following properties:

$$-\frac{1}{2}\hat{R}_L^1|\mathrm{Re}\Delta\psi\rangle + \frac{\sqrt{3}}{2}\hat{R}_L^1|\mathrm{Im}\Delta\psi\rangle = |\mathrm{Re}\Delta\psi\rangle \tag{45}$$

$$-\frac{\sqrt{3}}{2}\hat{R}_L^1|\mathrm{Re}\Delta\psi\rangle - \frac{1}{2}\hat{R}_L^1|\mathrm{Im}\Delta\psi\rangle = |\mathrm{Im}\Delta\psi\rangle. \tag{46}$$

Table S2. Transformations of (x, y, z), and $(\mathrm{Re}\Delta\psi, \mathrm{Im}\Delta\psi)$ under the threefold rotations $\hat{R}^n$ about z, and the spin matrices $\hat{R}^n_S$, corresponding to these rotations.

rotation	$\hat{R}^n_L(x,y,z)$	$\hat{R}^n_L(\mathrm{Re}\Delta\psi, \mathrm{Im}\Delta\psi)$	$\hat{R}^n_S$
$\hat{R}^1$	$(-\frac{1}{2}x - \frac{\sqrt{3}}{2}y, \quad \frac{\sqrt{3}}{2}x - \frac{1}{2}y, z)$	$(-\frac{1}{2}\mathrm{Re}\Delta\psi - \frac{\sqrt{3}}{2}\mathrm{Im}\Delta\psi, \quad \frac{\sqrt{3}}{2}\mathrm{Re}\Delta\psi - \frac{1}{2}\mathrm{Im}\Delta\psi)$	$\begin{pmatrix} e^{i\frac{\pi}{3}} & 0 \\ 0 & e^{-i\frac{\pi}{3}} \end{pmatrix}$
$\hat{R}^2$	$(-\frac{1}{2}x + \frac{\sqrt{3}}{2}y, -\frac{\sqrt{3}}{2}x - \frac{1}{2}y, z)$	$(-\frac{1}{2}\mathrm{Re}\Delta\psi + \frac{\sqrt{3}}{2}\mathrm{Im}\Delta\psi, -\frac{\sqrt{3}}{2}\mathrm{Re}\Delta\psi - \frac{1}{2}\mathrm{Im}\Delta\psi)$	$\begin{pmatrix} e^{i\frac{2\pi}{3}} & 0 \\ 0 & e^{-i\frac{2\pi}{3}} \end{pmatrix}$

These equations can be further rearranged as

$$\hat{R}^1_L|\mathrm{Re}\Delta\psi\rangle = -\frac{1}{2}|\mathrm{Re}\Delta\psi\rangle - \frac{\sqrt{3}}{2}|\mathrm{Im}\Delta\psi\rangle \tag{47}$$

$$\hat{R}^1_L|\mathrm{Im}\Delta\psi\rangle = \frac{\sqrt{3}}{2}|\mathrm{Re}\Delta\psi\rangle - \frac{1}{2}|\mathrm{Im}\Delta\psi\rangle. \tag{48}$$

Considering $\hat{R}^2$, one can find the following properties:

$$\hat{R}^2_L|\mathrm{Re}\Delta\psi\rangle = -\frac{1}{2}|\mathrm{Re}\Delta\psi\rangle + \frac{\sqrt{3}}{2}|\mathrm{Im}\Delta\psi\rangle \tag{49}$$

$$\hat{R}^2_L|\mathrm{Im}\Delta\psi\rangle = -\frac{\sqrt{3}}{2}|\mathrm{Re}\Delta\psi\rangle - \frac{1}{2}|\mathrm{Im}\Delta\psi\rangle. \tag{50}$$

Symmetrizing the matrix elements,

$$\vec{\boldsymbol{r}}_{ij} \to \frac{1}{3}\sum_{n=0}^{2} \hat{R}^n_L \vec{\boldsymbol{r}}_{ij}, \tag{51}$$

one can find that $\vec{\boldsymbol{r}}_{ij}$ will have the same form as for the C_4 group and given by Eq. (39).

Since $\mathrm{Re}\Delta\psi$ and $\mathrm{Im}\Delta\psi$ transform as, respectively, x and y (see Table II), like to the C_4 symmetry, one can assume that $\mathrm{Re}\Delta\psi \sim \cos\varphi$ and $\mathrm{Im}\Delta\psi \sim \sin\varphi$. This will yield again Eq. (41).

Like for the group C_4, it is straightforward to prove the orthogonality property: $\langle\mathrm{Re}\Delta\psi|\mathrm{Im}\Delta\psi\rangle = \langle\mathrm{Im}\Delta\psi|\mathrm{Re}\Delta\psi\rangle = 0$.

E. Triangular lattice

Consider the bond 01, which has the C_2 symmetry about y (the case of $CuFeO_2$ and MnI_2, see Figure S2 for notations). Therefore, the tensor $\vec{\boldsymbol{r}}_{01}$ should have the following form:

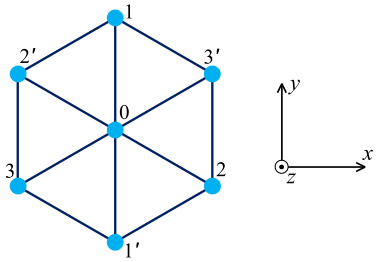


Figure S2. Fragment of triangular lattice with the notations of atomic sites around the central one (0). The sites 1, 2, and 3 are transformed to each other by the threefold rotations. The sites $1'$, $2'$, and $3'$ are related to, respectively 1, 2, and 3, by the spatial inversion.

$$\vec{\boldsymbol{r}}_{01} = \begin{pmatrix} r^{x,x} & 0 & r^{x,z} \\ 0 & r^{y,y} & 0 \\ r^{z,x} & 0 & r^{z,z} \end{pmatrix}. \tag{52}$$

Similar tensors in the bonds 02 and 03 can be obtained by the 120° rotations about z,

$$\hat{U} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{53}$$

as $\vec{\boldsymbol{r}}_{02} = \hat{U}\vec{\boldsymbol{r}}_{01}\hat{U}^T$ and $\vec{\boldsymbol{r}}_{03} = \hat{U}^T\vec{\boldsymbol{r}}_{01}\hat{U}$, which yields

$$\vec{\boldsymbol{r}}_{02} = \begin{pmatrix} \frac{1}{4}r^{x,x} + \frac{3}{4}r^{y,y} & -\frac{\sqrt{3}}{4}(r^{x,x} - r^{y,y}) & -\frac{1}{2}r^{x,z} \\ -\frac{\sqrt{3}}{4}(r^{x,x} - r^{y,y}) & \frac{3}{4}r^{x,x} + \frac{1}{4}r^{y,y} & \frac{\sqrt{3}}{2}r^{x,z} \\ -\frac{1}{2}r^{z,x} & \frac{\sqrt{3}}{2}r^{z,x} & r^{z,z} \end{pmatrix} \tag{54}$$

and

$$\vec{\boldsymbol{r}}_{03} = \begin{pmatrix} \frac{1}{4}r^{x,x} + \frac{3}{4}r^{y,y} & \frac{\sqrt{3}}{4}(r^{x,x} - r^{y,y}) & -\frac{1}{2}r^{x,z} \\ \frac{\sqrt{3}}{4}(r^{x,x} - r^{y,y}) & \frac{3}{4}r^{x,x} + \frac{1}{4}r^{y,y} & -\frac{\sqrt{3}}{2}r^{x,z} \\ -\frac{1}{2}r^{z,x} & -\frac{\sqrt{3}}{2}r^{z,x} & r^{z,z} \end{pmatrix}. \tag{55}$$

Furthermore, we have $\vec{\boldsymbol{r}}_{01'} = -\vec{\boldsymbol{r}}_{01}$, $\vec{\boldsymbol{r}}_{02'} = -\vec{\boldsymbol{r}}_{02}$, and $\vec{\boldsymbol{r}}_{03'} = -\vec{\boldsymbol{r}}_{03}$.

Without any symmetry [the case of $RbFe(MoO_4)_2$], we will have

$$\vec{\boldsymbol{r}}_{01} = \begin{pmatrix} r^{x,x} & r^{x,y} & r^{x,z} \\ r^{y,x} & r^{y,y} & r^{y,z} \\ r^{z,x} & r^{z,y} & r^{z,z} \end{pmatrix}, \tag{56}$$

$$\vec{\boldsymbol{r}}_{02} = \begin{pmatrix} \frac{1}{4}r^{x,x} + \frac{3}{4}r^{y,y} + \frac{\sqrt{3}}{4}(r^{x,y} + r^{y,x}) & \frac{1}{4}r^{x,y} - \frac{3}{4}r^{y,x} - \frac{\sqrt{3}}{4}(r^{x,x} - r^{y,y}) & -\frac{1}{2}r^{x,z} - \frac{\sqrt{3}}{2}r^{y,z} \\ \frac{1}{4}r^{y,x} - \frac{3}{4}r^{x,y} - \frac{\sqrt{3}}{4}(r^{x,x} - r^{y,y}) & \frac{3}{4}r^{x,x} + \frac{1}{4}r^{y,y} + \frac{\sqrt{3}}{4}(r^{x,y} + r^{y,x}) & -\frac{1}{2}r^{y,z} + \frac{\sqrt{3}}{2}r^{x,z} \\ -\frac{1}{2}r^{z,x} - \frac{\sqrt{3}}{2}r^{z,y} & -\frac{1}{2}r^{z,y} + \frac{\sqrt{3}}{2}r^{z,x} & r^{z,z} \end{pmatrix}, \tag{57}$$

and

$$\vec{\boldsymbol{r}}_{03} = \begin{pmatrix} \frac{1}{4}r^{x,x} + \frac{3}{4}r^{y,y} - \frac{\sqrt{3}}{4}(r^{x,y} + r^{y,x}) & \frac{1}{4}r^{x,y} - \frac{3}{4}r^{y,x} + \frac{\sqrt{3}}{4}(r^{x,x} - r^{y,y}) & -\frac{1}{2}r^{x,z} + \frac{\sqrt{3}}{2}r^{y,z} \\ \frac{1}{4}r^{y,x} - \frac{3}{4}r^{x,y} + \frac{\sqrt{3}}{4}(r^{x,x} - r^{y,y}) & \frac{3}{4}r^{x,x} + \frac{1}{4}r^{y,y} - \frac{\sqrt{3}}{4}(r^{x,y} + r^{y,x}) & -\frac{1}{2}r^{y,z} - \frac{\sqrt{3}}{2}r^{x,z} \\ -\frac{1}{2}r^{z,x} + \frac{\sqrt{3}}{2}r^{z,y} & -\frac{1}{2}r^{z,y} - \frac{\sqrt{3}}{2}r^{z,x} & r^{z,z} \end{pmatrix}. \tag{58}$$

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