Dzyaloshinskii-Moriya Interaction between Multipolar Moments in 5d$^1$ Systems

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We propose a new type of Dzyaloshinskii-Moriya interactions which act on high-rank multipole moments such as quadrupole and octupole moments. Here we consider the 5d$^1$ systems with broken spacial inversion symmetry, where the interplay of electron correlation, spin-orbit coupling, and inversion symmetry breaking plays a crucial role. Using numerical diagonalization on a two-site multiorbital Hubbard model, we reveal that anti-symmetric products of multipole operators have finite expectation values, indicating the existence of Dzyaloshinskii-Moriya interactions for multipoles. We also find that these expectation value have unusual dependence on a spin-orbit coupling.

**Introduction.** Interplay of electron correlation and strong spin-orbit coupling (SOC) has attracted much interest due to its novel physical properties. For electrons in d orbitals, the SOC becomes larger as the main quantum number increases from 3d to 4d, and to 5d. In 5d-based compounds, SOC becomes even comparable with electron correlation. Thus, they offer an ideal field to investigate the interplay of them.

Recently, 5d$^5$ systems such as Ir-based magnets have been actively studied. Examples include Sr$_2$IrO$_4$, which shows an unconventional metal-insulator transition, and Na$_2$IrO$_3$, which is proximity to the Kitaev spin liquid. In these materials, Ir$^{4+}$ ion is located at the center of the octahedral structure, thus fivefold 5d orbitals are split into threefold $t_{2g}$ orbitals and twofold $e_g$ orbitals by the crystalline electric field. Then, in the presence of strong SOC, the $t_{2g}$ orbitals with pseudo orbital degrees of freedom ($L_{eff} = 1$) form upper $J_{eff} = 1/2$ doublet and lower $J_{eff} = 3/2$ quartet, and only half-filled $J_{eff} = 1/2$ doublet is active for 5d$^5$ systems.

In contrast to 5d$^5$ systems, $J_{eff} = 3/2$ quartet becomes active in 5d$^1$ systems. Remarkably, the exchange interactions between $J_{eff} = 3/2$ states contain not only a quadratic operator in $J_{eff}$, but also biquadratic and triquadratic operators, due to its fourfold degree of freedoms. Indeed, these interactions induce many exotic phases such as the quadrupolar ordered phase in a double-perovskite material Ba$_2$NaOsO$_6$.

It is even more interesting if we consider the effects of spacial inversion symmetry breaking (ISB). If the system has magnetic dipole moments, the lack of spacial inversion symmetry induces the anti-symmetric exchange interaction, i.e. the Dzyaloshinskii-Moriya (DM) interaction. For 3d systems, the DM interaction has been evaluated precisely by first principles calculations. On the other hand, for 5d$^1$ systems, which have the higher-rank multipole degrees of freedom, we naturally expect that there exist the analogues of DM interactions for the higher-rank multipoles, which can lead to novel phases with chiral multipole orders.

In this letter, we study exchange interactions between multipole moments by using numerical exact diagonalization method on two-site systems with three $t_{2g}$ orbitals for each site. We discuss the perovskite crystal with the corner-sharing and the edge-sharing configurations, shown in Figs. 1(a) and 1(b), respectively, and ISB is taken into account through the displacement of oxygen sites. We show the existence of DM interaction between the dipoles of $J_{eff} = 3/2$, as well as between higher-rank multipoles that consist of products of $J_{eff}$ operators. To do this, we compute the expectation values of anti-symmetric products of multipole operators as a function of the SOC.

**Model and method.** We consider the two-site problem

![Fig. 1.](Image) (Color online) Schematic pictures of (a) corner-sharing configuration and (b) edge-sharing configuration. Blue circles denote 5d$^1$ ions and light blue circles denote oxygen ions.
for 5\textsuperscript{d\textup{}} systems. The Hamiltonian is given as

\begin{equation}
H = H_t + H_{\text{ISB}} + H_{\text{int}} + H_{\text{SO}},
\end{equation}

where \( H_t \), \( H_{\text{ISB}} \), \( H_{\text{int}} \), and \( H_{\text{SO}} \) represent the Hamiltonians of transfer integrals between \( t_{2g} \) orbitals for inversion-symmetric systems, transfer integrals induced by ISB, on-site Coulomb interactions, and SO, respectively. The total electron number is set as two. As for the lattice structure, we study the perovskite crystal of the corner-sharing [Fig. 1(a)] and edge-sharing [Fig. 1(b)] configurations. The two-site systems considered here are encircled by red dotted lines in the same figures. As we will explain, the difference of lattice structure is reflected to the difference of oxygen-mediated transfer integrals in \( H_t \).

For simplicity, we ignore the direct transfer integrals between \( d \) orbitals (\( t_{4d} \)), and consider the oxygen-mediated transfer integrals, shown in Figs. 2(a) and Figs. 2(b). As a result, \( H_t \) is given by

\begin{equation}
H_t^{(a)} = \sum_{\sigma = \uparrow, \downarrow} t(1, \sigma, \alpha) d_{1, \alpha, \sigma} d_{2, \alpha, \sigma} + d_{1, \alpha, \sigma} d_{2, \alpha, \sigma} + h.c.,
\end{equation}

for a corner-sharing configuration, and

\begin{equation}
H_t^{(b)} = \sum_{\sigma = \uparrow, \downarrow} t(1, \sigma, \alpha) d_{1, \alpha, \sigma} d_{2, \alpha, \sigma} + d_{1, \alpha, \sigma} d_{2, \alpha, \sigma} + h.c.,
\end{equation}

for an edge-sharing configuration. Here, \( d_{1, \alpha, \sigma}(d_{1, \alpha, \sigma}^\dagger) \) is a creation (annihilation) operator of the \( \ell \)-th orbital (\( \ell = 1, 2, \) and 3 indicate \( y, z, \) and \( xy \) orbitals, respectively) with spin \( \sigma \) at the \( i \)-th site, and \( t \) is the amplitude of transfer integrals derived from the transfer integrals between \( d \) and \( p \) orbitals.

In addition to the above transfer integrals, we also consider transfer integrals, \( H_{\text{ISB}} \), induced by the distortion of oxygen atoms [Figs. 3(a) and 3(b)]. To be specific, we consider the situation where the oxygen between the two \( 5\text{d} \) atoms shifts slightly in the \( z \)-direction, giving rise to ISB of the system\textsuperscript{14-17}. Then, new hopping processes appear which involve \( d_{xy} \) orbitals; they are given by

\begin{equation}
H_{\text{ISB}}^{(a)} = \sum_{\sigma = \uparrow, \downarrow} t'(1, \sigma, \alpha) d_{1, \alpha, \sigma} d_{2, \alpha, \sigma} + d_{1, \alpha, \sigma} d_{2, \alpha, \sigma} + h.c.,
\end{equation}

for a corner-sharing configuration, and

\begin{equation}
H_{\text{ISB}}^{(b)} = \sum_{\sigma = \uparrow, \downarrow} t'(1, \sigma, \alpha) d_{1, \alpha, \sigma} d_{2, \alpha, \sigma} + d_{1, \alpha, \sigma} d_{2, \alpha, \sigma} + h.c.).
\end{equation}

for an edge-sharing configuration. Microscopic derivation of \( t' \) and \( t'' \) can be straightforwardly carried out by using the Slater-Koster formalism\textsuperscript{16,18}.

The rest two terms, \( H_{\text{int}} \) and \( H_{\text{SO}} \), are given by

\begin{align}
H_{\text{int}} &= U_d \sum_{i=1,2} n_{i,\sigma,\uparrow} n_{i,\sigma,\downarrow} + \frac{U_d}{2} \sum_{i=1,2} \sum_{l,m \sigma} n_{i,\sigma,\uparrow} n_{i,\sigma,\downarrow} + \frac{U_d}{2} \sum_{i=1,2} \sum_{\sigma \neq \sigma'} n_{i,\sigma,\uparrow} n_{i,\sigma',\downarrow},
\end{align}

and

\begin{align}
H_{\text{SO}} &= \frac{\zeta}{2} \sum_{i=1,2} \sum_{\sigma,\sigma'} \epsilon_{\sigma,\sigma'} d_{i,\sigma,\sigma'} d_{i,\sigma',\sigma} + h.c.,
\end{align}

where \( n_{i,\sigma,\sigma'} \) is number operator defined as \( n_{i,\sigma,\sigma'} = d_{i,\sigma,\sigma'}^\dagger d_{i,\sigma,\sigma'} \).
ues are finite, there exist corresponding interactions in the effective Hamiltonian that makes those expectation values finite. Possible single-site multipole operators for \( J_{\text{eff}} = 3/2 \) states are summarized in Table I.  

| Multipole | Symmetry | Operator |
|-----------|----------|----------|
| Dipole    | \( T_{1u} \) | \( J_x, J_y, J_z \) |
| Quadrupole| \( T_{2g} \) | \( Q_x = [J_yJ_z] / 2 \) |
|           |           | \( Q_y = [J_xJ_z] / 2 \) |
|           |           | \( Q_z = [J_xJ_y] \) |
|           |           | \( E_y = (J_y^2 - J_z^2 - J_x^2) / \sqrt{3} \) |
| Octupole  | \( A_{2u} \) | \( O_x = J_z^2 - 1/2 \) \(| [J_xJ_yJ_z] + [J_zJ_xJ_y] | \) |
|           | \( T_{1u} \) | \( O_y = J_x^2 - 1/2 \) \(| [J_xJ_yJ_z] + [J_yJ_xJ_z] | \) |
|           | \( T_{2u} \) | \( O'_y = \sqrt{15} / 6 \) \(| [J_xJ_yJ_z] - [J_zJ_xJ_y] | \) |

Next, before discussing the DM interactions between multipole operators, let us see the DM interaction for dipoles. We show in Fig. 5(a) \( \zeta \) dependence of the expectation value \( \langle J_1 \cdot \hat{\mathbf{z}} \times \mathbf{J}_2 \rangle_y \) for \( t'/t = 0.01, 0.05 \) and 0.1, where \( J_i \) \( \hat{\mathbf{z}} \) \((i = 1, 2) \) indicates the \( J_{\text{eff}} = 3/2 \) state at \( i \)-th site. Note that components other than \( y \) is 0 due to the symmetry requirement. In other words, the direction of \( \mathbf{D} \) vector is determined by setting a lattice structure and a bond direction. Indeed, the expectation value \( \langle J_1 \cdot \hat{\mathbf{z}} \times J_2 \rangle_y \) is finite for all values of \( \zeta \), indicating that the DM interaction between \( J \) is induced by \( \text{HS} \). Such a DM interaction of \( J \) also emerges in 5d systems with broken inversion symmetry.  

![Fig. 4.](image)  

This Hamiltonian is the origin of the finite expectation value of \( \langle L_1 \times L_2 \rangle_y \) and \( \langle Q_1 \times Q_2 \rangle_y \). The results in Fig. 5(a) indicates that the SOC enhances the DM interactions of orbital part, \( L_1 \times L_2 \), for small SOC regime.

To compare the contributions from spin and orbital parts, we plot the spin part of the DM interaction, \( \langle S_1 \times S_2 \rangle_y \), together with the total one in Fig. 5(b).

Now, let us move on to the DM interactions for higher-rank multipoles. Figure 5(c) shows \( \zeta \) dependence of the anti-symmetric product of quadrupoles, \( \langle Q_1 \times Q_2 \rangle y \), for \( t'/t = 0.01, 0.05 \) and 0.1. (\( Q_1 \) indicates the quadrupole moment with \( T_{2g} \) symmetry at \( i \)-th site; see Table I.) It is found that \( \langle Q_1 \times Q_2 \rangle y \) is finite for both of two configurations (except for \( \zeta/t > 3.5, t'/t = 0.05, 0.1 \) for an edge-sharing configuration). This indicates that there exist quadrupole DM interactions, which are novel DM interactions among 5d systems.

We remark that the quadrupolar DM interaction is generally expected to lead to the lattice distortion beyond the mere displacement of oxygens, through the and octupolar DM interactions.

Interestingly, \( \langle J_1 \cdot \hat{\mathbf{z}} \times J_2 \rangle_y \) is nonzero even at \( \zeta/t = 0 \). This is because the orbital part, \( \langle L_{1,\text{eff}} \times L_{2,\text{eff}} \rangle_y \), is finite due to the lattice distortion. To see this, we employ a perturbation theory with respect to \( H_{1} + \text{HS} \) at \( \zeta = 0 \). For simplicity, we use \( H_{\text{int}} = U \sum_{i=1,2} \sum_{m: i \neq m} n_i n_{i+m} \) as interaction term. Assuming that \( U \gg t, t' \), we perform a second-order perturbation to obtain effective multipole-multipole interactions. As a result, we obtain

\[
H \sim \frac{t't''}{U} \left( L_1 \times L_2 \right)_y - \frac{4t't''}{U} \left( Q_1 \times Q_2 \right)_y + (\text{other interactions}).
\]
change of the charge distribution. In this letter, we discuss only the electronic state under fixed lattice structure, and lattice distortion induced by quadrupole DM interaction is the future problem.

The octupolar terms, \( (O_{1} \times O_{1}^{'})_y \), is found to be finite and have similar \( \zeta \) dependence to that for the quadrupole. \( (O_{1}^{'}) \) indicates the octupole moment with \( T_{2u} \) symmetry at \( i \)-th site; see Table 1. The only sharp difference is that octupolar DM interaction becomes exactly zero at \( \zeta/t = 0 \). This is because the highest rank of multipole moment \( b_{3} \) for \( \mathcal{L}_{\text{eff}} \) is quadrupole, thus an octupole does not emerge at \( \zeta/t = 0 \).

Before closing this section, we discuss the reason why \( (Q_{1} \times Q_{2})_y \) and \( (O_{1} \times O_{1}^{'})_y \) vanish in the large SOC region in the edge sharing system with small distortion. In this region, we can calculate the wave function of the ground state. It is denoted as

\[
|\text{GS}\rangle = a e^{i \frac{\pi}{2} \left( \frac{3}{2} \frac{1}{2} \right) \left( \frac{1}{2} \frac{3}{2} \right) - \frac{1}{2} \frac{3}{2} \left( - \frac{3}{2} - \frac{1}{2} \right) - \frac{b}{(3 \frac{1}{2} - \frac{1}{2}) + \frac{1}{2} \frac{3}{2} - \frac{3}{2} \frac{1}{2} (\frac{1}{2} \frac{3}{2} - \frac{3}{2} \frac{1}{2}) .}
\]

Here, we use the basis \(|J_{1z}, J_{2z}\rangle\). The parameters \( a \) and \( b \) are independent of SOC, and \( b \) increases with lattice distortion. By using this state, it is found that \( \langle J_{1} \times J_{2} \rangle_y = 48 \sqrt{2} a b / 25 \), and \( \langle Q_{1} \times Q_{2} \rangle_y = \langle O_{1} \times O_{1}^{'})_y \rangle = 0 \). For example, in the \( t'/t = 0.01 \) case, we found \( a \simeq 0.46, b \simeq 0.02 \). Thus, we can estimate \( \langle J_{1} \times J_{2} \rangle_y \simeq 0.25 \) and this is consistent with the result of numerical calculation. From this calculation, it is found that if the wave function has symmetric form such as Eq. (7), multipolar DM interactions can be exactly zero even though the lattice is distorted.

**Concluding remarks.** In conclusion, we have introduced the new type of DM interactions, namely the quadrupolar and octupolar DM interactions, on 5d3 systems with the structures of edge-sharing octahedra and corner-sharing octahedra. These novel DM interactions may serve as a source of chiral multipolar orders, which have not yet been observed experimentally. Therefore, search for candidate materials for that will be an intriguing future problem. For instance, KTaO\(_3\) with vacancy of oxygens has an inversion symmetry broken perovskite configuration,\(^{22}\) and thus will be a good candidate. Another possibility is to make a surface/interface of 5d\(^3\) perovskite material,\(^{16,17}\) on which ISB is artificially introduced.

Finally, we focus on the Mott insulating phase in this work, and the comparison with itinerant systems\(^{23-25}\) will be an interesting perspective.

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