Theoretical Prediction of the Nematic Orbital-Ordered State in Ti-Oxypnictide Superconductor BaTi$_2$(As,Sb)$_2$O

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The electronic nematic state without magnetization emerges in various strongly correlated metals such as Fe-based and cuprate superconductors. To understand this universal phenomenon, we focus on the nematic state in Ti-oxypnictide BaTi$_2$(As,Sb)$_2$O, which is expressed as the three-dimensional 10-orbital Hubbard model. The antiferromagnetic fluctuations are caused by the Fermi surface nesting. Interestingly, we find the spin-fluctuation-driven orbital order due to the strong orbital-spin interference, which is described by the Aslamazov-Larkin vertex correction (AL-VC). The predicted intra-unit-cell nematic orbital order is consistent with the recent experimental reports on BaTi$_2$(As,Sb)$_2$O. Thus, the spin-fluctuation-driven orbital order due to the AL-VC mechanism is expected to be universal in various two- and three-dimensional multiorbital metals.

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I. INTRODUCTION

Various interesting symmetry breaking phenomena associated with the charge, orbital, and spin degrees of freedom emerge in strongly correlated electron systems. Among them, the rotational symmetry breaking, so-called the nematic transition, has attracted increasing attention, after the discovery of the nematic order in Fe-based and cuprate superconductors. In Fe-based superconductors, both the spin-nematic order [1–4] and the orbital order [5–11] are considered as the origin of the nematic order. In cuprates, the $p$-orbital order is a promising candidate for the nematic [12, 13], whereas other promising scenarios had been proposed so far [14–17]. The nematic transitions in these superconductors cannot be understood within the random-phase-approximation (RPA) based on the Hubbard models, so it is demanded to develop the microscopic theory beyond the mean-field-level approximations.

To achieve the fundamental understanding of the electronic nematic states, we focus on the nematic phase in the Ti-oxypnictide superconductors [18–21]. No magnetic order appears in the nematic phase [22, 23], similarly to FeSe. The nematic order in Ti-oxypnictides is driven by the electron-interaction since the orthorhombic lattice deformation $(a-b)/(a+b)$ is just $\sim 0.1\%$ [24], which is even smaller than that in Fe-based superconductors. In contrast to these systems, the lattice distortions in Jahn-Teller systems (like Mn-oxides) reach a few %. The nematic order in BaTi$_2$As$_2$O is ascribed to the intra-unit-cell charge-density-wave (CDW) with $d$-wave symmetry since no superlattice was found by the electron diffraction studies [24, 25]. This result is analogous to the “$d$-symmetry CDW” in under-doped cuprates in Refs. [12, 13, 26]. Such intra-unit-cell CDW in Ti-oxypnictide is unable to be explained by the electron-phonon mechanism [27]. Thus, the study of Ti-oxypnictides should serve to understand the origin of the nematicity due to the electron-interaction.

Interestingly, the superconducting phase (with $T_c \sim 5K$) is realized near the nematic phase in various Ti-oxypnictides, indicating the importance of the nematic fluctuations on the superconductivity. In addition, strong antiferromagnetic (AFM) spin fluctuations appear near the nematic phase in BaTi$_2$Sb$_2$O [22], analogously to the Fe-based and cuprate superconductors. Therefore, Ti-oxypnictides would give us great hints to understand the close interplay between the nematicity, magnetism, and superconductivity, which is a central issue in Fe-based and cuprate superconductors.

In this paper, we study the origin of the non-magnetic nematic order in Ti-oxypnictides based on the realistic Hubbard model for BaTi$_2$(As,Sb)$_2$O. Due to the Fermi surface (FS) nesting, the AFM fluctuations develop at $Q_s = (\pi, 0, \pi)$ and $(0, \pi, \pi)$, consistently with the previous theoretical studies [28, 29] and the NMR study [22]. Remarkably, we find that the strong orbital fluctuations on the superconductivity. In addition, the orbital-order/fluctuations and magnetic-order/fluctuations simultaneously emerge. Such Kugel-Khomskii-type orbital-spin interplay is explained by the AL-VC in the weak-coupling picture.

The AL-VC represents the orbital-spin interplay, which is intuitively understood in terms of the strong-coupling picture $U \gg W_{\text{band}}$ as we explained in Ref. [9]: In Fe-based superconductors, the ferro-orbital order $n_{xz} \gg n_{yz}$ gives rise to the strong anisotropy in the nearest-neighbor exchange interaction, $J^{(1)}_z \neq J^{(1)}_y$, and therefore the stripe AFM order with is induced. Thus, the orbital-order/fluctuations and magnetic-order/fluctuations simultaneously emerges. Such Kugel-Khomskii-type orbital-spin interplay is explained by the AL-VC in the weak-coupling picture.
II. MODEL HAMILTONIANS

Figures 1 (a) and (b) show the metallic Ti$_2$Pn$_2$O-layer in Ti-oxypnictides (Pn=As, Sb). The unit cell contains two Ti-sites and two Pn-sites. The bandstructure near the Fermi level is mainly composed of $(d_{x^2-y^2}, d_{xy})$-orbitals on Ti-A and $(d_{y^2-z^2}, d_{xy})$-orbitals on Ti-B, which are respectively denoted as (1, 2) and (3, 4) hereafter. Here, we perform the band calculation of BaTi$_2$Pn$_2$O using the WIEN2K software. In Fig. 1, we show the FSs for (c) BaTi$_2$As$_2$O and the FSs for (d) BaTi$_2$Sb$_2$O obtained by the band calculation.

The multiorbital Coulomb interaction term is given as

$$H_M^{U,U'} = \frac{1}{2} \sum_{i,l,\sigma \neq \sigma'} U n_{i,l,\sigma} n_{i,l,\sigma'} + \frac{1}{2} \sum_{i,l \neq m, \sigma, \sigma'} \left\{ U'n_{i,l,\sigma} n_{i,m,\sigma'} + J_{m,l} c_{i,m,\sigma}^\dagger c_{i,l,\sigma'} + c_{i,m,\sigma}^\dagger c_{i,l,\sigma'} \delta_{\sigma,\sigma'} \right\}, \quad (1)$$

where $U$ and $U'$ are the intra-orbital and inter-orbital Coulomb interactions, and $J$ is the Hund’s interactions for $d$-electrons. Hereafter, we assume the relation $U = U' + 2J$ and $J > 0$, and fix the ratio $J/U = 1/9$ except in Fig. 5 (d). We verified that similar numerical results are obtained for $J = 1/8$. In the case of Fe-based superconductors, $J/U$ ranges from 0.0945 (in FeSe) to 0.134.
(in LaFeAsO) according to the detailed and exhaustive first-principles study in Ref. [30].

III. THEORETICAL ANALYSIS

Based on the obtained model, we calculate the spin and orbital susceptibilities. The bare susceptibility \( \chi^{s,0}(q) = -T \sum_k G_{l,m}(k+q)G_{m',l'}(k) \), where \( l,m \) are the orbital indices, \( k = (k, \epsilon_n) \) and \( q = (\mathbf{q}, \omega) \); \( \epsilon_n = \pi(2n + 1)T \) is the fermion (boson) Matsubara frequency. \( \tilde{G}(k) = (\mu - \tilde{h}(k))^{-1} \) is the Green function, where \( \tilde{h}(k) \) is the kinetic term in the orbital basis. The charge (spin) susceptibility is

\[
\chi^{c(s)}(q) = (1 - \Phi^{c(s)}(q) \tilde{\Gamma}^{c(s)} - 1 \Phi^{c(s)}(q),
\]

where \( \Phi^{c(s)}(q) = \chi^{0}(q) + \chi^{c(s)}(q) \) is the charge (spin irreducible susceptibility, and \( \chi^{c(s)}(q) \) is VC for the charge (spin) channel: \( \chi^{c}(q) \) gives the important orbital-spin interference although it is dropped in the RPA [8]. \( \Gamma^{c(s)}(q) \) is the d-orbital bare Coulomb interaction for the charge (spin) channel, composed of the on-site Coulomb interactions \( U, U' \) and \( J [8] \). In a single-orbital model, \( \tilde{\Gamma}^{c(s)} \) is simply given as \( \Gamma^{c} = U \) and \( \Gamma^{s} = -U \).

The charge (spin) susceptibility diverges when the charge (spin) Stoner factor \( \alpha_{C(s)} \), which is given by the maximum eigenvalue of \( \Phi^{c(s)}(q) \Gamma^{c(s)} - 1 \Phi^{c(s)}(q) \), reaches unity. With increasing \( U \) under the condition \( J/U = 1/9 \), both \( \alpha_{C} \) and \( \alpha_{S} \) increase monotonically, and the orbital order (magnetic order) occurs when \( \alpha_{C} = 1 \) (\( \alpha_{S} = 1 \)). In the RPA, in which the susceptibility is given as \( \chi^{c(s),\text{RPA}}(q) = (1 - \Phi^{c(s)}(q) \tilde{\Gamma}^{c(s)} - 1 \Phi^{c(s)}(q) \), the relation \( \alpha_{S} > \alpha_{C} \) is always satisfied for a positive \( J [8] \). Therefore, for \( J/U \sim O(10^{-1}) \), \( \chi^{c,\text{RPA}}(q) \) remains small even when \( \chi^{c,\text{RPA}}(Q_s) \) diverges.

A. RPA analysis for the spin susceptibility

First, we explain the RPA results obtained by using \( 32 \times 32 \times 8 \) \( k \)-meshes and 256 Matsubara frequencies. We fix the temperature at \( T = 50 \) meV. Figure 3 shows the spin susceptibility in the RPA: \( \chi^{s,\text{RPA}}_{l,m}(q) = \chi^{s,\text{RPA}}_{l,m}(q) \), for (a) \( l = m = 1 \) and (b) \( l, m = (1, 2) \) at \( q_z = \pi \) in the case of \( U = 2.06 \) eV and \( J/U = 1/9 \) (\( \alpha_{S} = 0.98 \)). They have sharp peaks at \( q = (\pi, 0, 0) \) and \( (0, \pi, 0) \). (Note that \( \chi^{s,\text{RPA}}_{l,m}(q) \) is very small for \( l, l' \leq 2 \) and \( m, m' \geq 3 \)). The strong spin fluctuations are actually observed in BaTiGdSB\(_2\)O by NMR measurement above the structure transition temperature \( T_{\text{c}} \) [22]. However, the charge susceptibility remains very small in the RPA, as we show \( \chi^{c,\text{RPA}}_{l,m}(q) \) in Fig. 3 (c). Thus, the experimental nematic order cannot be explained by the RPA.

B. Analysis of the Aslamazov-Larkin Vertex Correction for the orbital susceptibility

In the next stage, we study the charge susceptibility by taking the AL-VC into account, and derive the intra-unit-cell orbital order. In various two-dimensional multiorbital metals such as Fe-based and cuprate superconductors, the spin-fluctuation-driven orbital order and fluctuations are realized due to the large AL-VC for the charge channel [8, 31, 32]. In this mechanism, very weak spin fluctuations give rise to the orbital order when the ratio \( J/U \) is small, as observed in FeSe with \( J/U \approx 0.1 \) [33, 35, 36]. However, it is highly nontrivial whether the AL-VC is important or not in three-dimensional systems like Ti-oxypnictides. In this paper, we calculate the AL-VC in the three-dimensional model for the first time. We neglect the AL-VC for the spin channel and the Maki-Thompson VC's since they are negligible in various models [8, 12, 13, 33]. We drop the feedback effect from \( \tilde{\chi}^{c} \) to \( X^{c} \) since its smallness has been verified in the present model, similarly to the case of the \( d-p \) Hubbard model for cuprates [12]. The expression for the AL-VC is given in Appendix A.

We present the numerical results obtained by including the AL-VC. The Stoner factors are \( (\alpha_{C}, \alpha_{S}) = (0.99, 0.98) \) for \( U = 2.06 \) eV and \( J/U = 1/9 \) at \( T = 50 \) meV. Figure 4 (a) shows the susceptibility of the orbital polarization at Ti-A site,

\[
\chi_{\text{orb}}^{A}(q) = \sum_{l,m=1}^{2} \chi_{l,m}^{A}(q) \cdot (-1)^{l+m} = \chi_{1;1}^{A}(q) + \chi_{2;2}^{A}(q) - 2\chi_{1;2}^{A}(q), \tag{3}
\]

at \( q_z = 0 \). We see that the strong ferro-orbital fluctuations appear due to the AL-VC, which are absent in the RPA result in Fig. 3 (c). In contrast, the susceptibility of the charge density at Ti-A site, \( \chi_{\text{charge}}^{A}(q) = \sum_{l,m=1}^{2} \chi_{l,m}^{A}(q) = \chi_{1;1}^{c}(q) + \chi_{2;2}^{c}(q) + 2\chi_{1;2}^{c}(q), \) re-
4 is discussed in Ref. [12]. The obtained form factor for Fig. ± proportional to vector of \( \hat{\Phi} \) tional to the form factor \( \chi \) orbital polarization. (c) \( \chi \) der (∆). (d),(e) Schematic intra-unit-cell nematic orbital order for simplicity, since the net charge at Ti-A and that at Ti-B are almost equivalent.

mains small as shown in Fig. 4 (a). These results means the emergence of the intra-site orbital polarization, \( \Delta n_1, \Delta n_2 < 0 \) at Ti-A and \( \Delta n_3, \Delta n_4 < 0 \) at Ti-B, as schematically shown in Fig. 4 (b). Here, \( \Delta n_i \) is the modulation of the electron density on orbital \( i \).

In addition, the inter-site orbital susceptibility between Ti-A and Ti-B,

\[
\chi^{A-B}(q) = \sum_{l,m=1}^{2} \chi^{c}_{l,m+2}(q) \cdot (-1)^{l+m} = \chi^{c}_{1,3}(q) + \chi^{c}_{2,4}(q) - \chi^{c}_{1,4}(q) - \chi^{c}_{2,3}(q),
\]

has large negative peak at \( q = 0 \) as we show in Fig. 4 (c). In contrast, the inter-site charge susceptibility \( \chi^{A-B}(q) \equiv \sum_{l,m=1}^{2} \chi^{c}_{l,m+2}(q) \) is not enhanced at all. These results mean that the orbital polarization in the ordered state, \( \Delta n \equiv (\Delta n_1, \Delta n_2, \Delta n_3, \Delta n_4) \), is roughly proportional to \( \pm (1, -1, -1, 1) \).

More properly, the orbital polarization \( \Delta n \) is proportional to the form factor \( f \), which is given by the eigenvector of \( \hat{\Phi}(q) \Gamma^c \) for the largest eigenvalue \( \alpha_s \), as we discussed in Ref. [12]. The obtained form factor for Fig. 4 is \( f = \pm (1.06, -0.94, -1.06, 0.94) \). Thus, the predicted orbital pattern are shown in Fig. 4 (d) or (e): When the electron densities for orbitals 1 and 4 in Fig. 4 (d) increase, the densities for other orbitals in (e) decrease. The predicted intra-unit-cell orbital order is consistent with the absence of the superlattice in BaTi\(_2\)(As,Sb)\(_2\)O in the nematic phase reported by the electron diffraction study [24, 25].

The charge pattern in Fig. 4 (d),(e) may be safely called orbital-selective charge order, since it is the spontaneous symmetry breaking among degenerate orbitals on different sites. (Two orbitals on the same Ti-ion are non-degenerated.) However, we call this charge pattern the orbital order for simplicity, since the net charge at Ti-A and at Ti-B are almost equivalent.

C. Explanation for the intra-unit-cell orbital order due to the AL-VC

Here, we verify numerically that the intra- and inter-orbital fluctuations in Fig. 4 originate from the diagonal elements of the AL-VC, \( X^{c}_{l,l}(0) \) with \( l = 1 \sim 4 \). For \( U = 2.06 \) eV, the diagonal elements of the AL-VCs are shown in Figs. 5 (a) and (b), in which \( X^{c}_{1,1}(0) = 0.84 \) and \( X^{c}_{2,2}(0) = 0.49 \) respectively. Then, the irreducible susceptibilities are \( \Phi_{1,1}(0) = 1.21 \) and \( \Phi_{2,2}(0) = 0.75 \). By taking only the diagonal AL-VCs into account in \( \Phi^c \), strong orbital fluctuations with the form factor \( f = \pm (1.04, -0.96, -1.04, 0.96) \) appears at \( U \approx 2.0 \) eV.

Next, we present a mathematical explanation why the strong orbital fluctuations with the form factor \( f \propto (1, -1, -1, 1) \) are obtained, which corresponds to the intra-unit-cell orbital order. To understand this nontrivial result, we put \( \Phi_{1,1}(0) = \Phi \) for \( l = 1,3 \) and \( \Phi_{2,2}(0) = (1-x) \cdot \Phi \) for \( l = 2,4 \), and other elements are zero for simplicity. We also put \( U = U' \) and \( J = 0 \) for simplicity. Under this simplification, the largest eigenvalue of \( \Phi^c(q) \Gamma^c \) is doubly degenerate, and the corresponding form factors are \( f_1 \propto (y, -1, -y, 1) \) and \( f_2 \propto (y, -1, y, -1) \), where

FIG. 4: (color online) (a) \( \chi^{A}(q) \) and \( \chi^{B}(q) \) at \( q_x = 0 \) obtained by including the AL-VC. We put \( U = 2.06 \) eV and \( J/U = 1/9 \). (b) Schematic intra-site orbital polarization. (c) \( \chi^{A}(q) \) and \( \chi^{B}(q) \) at \( q_x = 0 \). (d),(e) Schematic intra-unit-cell nematic orbital order \( (\Delta n_1, \Delta n_2, \Delta n_3, \Delta n_4) \propto \pm (1, -1, -1, 1) \), which triggers the orthorhombic structural transition.

FIG. 5: (color online) (a),(b) Obtained AL-VCs \( X^{c}_{1,1}(0) \) and \( X^{c}_{2,2}(0) \) at \( q_x = 0 \) for \( J/U = 1/9 \). (c) \( \alpha_c(q_x) \) for \( J/U = 1/9 \) and (d) \( \alpha_c(q_x) \) for \( J/U = 1/8 \) as functions of \( \alpha_s \).
$y \approx 1 + x/4$ for $|x| \ll 1$, as we explain in Appendix B. This degeneracy of the form factor is lifted by the small inter-site components of $\Phi_{\text{inter}}(0)$ with $l \leq 2$ and $n \geq 3$. In the present model, the form factor $f_1$ is selected mainly due to the negative $X'_{\text{inter}}(0)$, as explained in Appendix B. Therefore, the intra-unit-cell orbital order with $f_1 \approx (1, -1, -1, 1)$ is stably obtained without tuning model parameters.

In the present theory, the charge Stoner factor $\alpha_C$ is enlarged by the AL-VC, and the AL-VC increases near the magnetic critical point. Figures 5 (c) and (d) shows enlarged by the AL-VC, and the AL-VC increases near $D$ in contrast, and the uniform susceptibility is suppressed [18, 19]. Therefore, the intra-unit-cell orbital order should trigger the experimental orthorhombic structure transition at $T = T_S$.

D. Pseudo-gap formation in the orbital-ordered state

Below, we discuss the electronic states in the ordered state below $T_S$, by introducing the orbital-dependent potential energy $\Delta E_l$ ($l \approx 1 \sim 4$). The potential energy for the intra-unit-cell orbital order in Fig. 4 (d) or (e) is $\Delta E_{\text{orbital}} \equiv (\Delta E, -\Delta E, -\Delta E, \Delta E)$. In addition, we also discuss the intra-unit-cell charge order $\Delta E_{\text{charge}} \equiv (\Delta E, \Delta E, -\Delta E, -\Delta E)$. This possibility had been discussed in Ref. [24]. We note that the orbital-ordered state in Fe-based superconductors ($n_{xz} \neq n_{yz}$) had been explained theoretically, by developing the self-consistent vertex correction (SC-VC) theory for the orbital-ordered state [39], and the experimental orbital polarization $E_{yz} - E_{xz}$ is $50 \sim 60$ meV.

Figure 6 shows the DOS, $D(e)$, in the (a) orbital-ordered state and (b) charge-ordered state for $\Delta E = 0 \sim 0.4$ eV. To make comparison with experiments qualitatively, $\Delta E$ should be multiplied with the renormalization factor due to the self-energy, $\tilde{z} \equiv m_{\text{band-cal}}/m^* (< 1)$, although the value of $\tilde{z}$ is unknown in Ti-oxypnictides. (Note that $z^{-1} \approx 2 \sim 10$ in Fe-based superconductors.) In (a), the DOS at the Fermi level, $D(0)$, decreases with $\Delta E > 0$, and the pseudo-gap structure appears. In (b), in contrast, $D(0)$ is almost independent of $\Delta E$. The reason for the pseudo-gap formation in (a) is that both the electron-like FS around M point and hole-like FS around X point shrink with $\Delta E$, whereas only the latter shrinks in (b). The striking difference in the FS deformation is understood from the orbital character of the electron-like FS, as we discuss in Appendix C.

In Fig. 6 (c), we show the DOS for $\Delta E \equiv (\Delta E, 0, -\Delta E, 0) = (\Delta E_{\text{orbital}} + \Delta E_{\text{charge}})/2$, which is also a possible nematic state suggested experimentally [24].

Experimentally, below $T_S$, the resistivity shows the upturn, and the uniform susceptibility is suppressed [18, 19]. Also, a pseudo-gap formation is indicated by ARPES below $T_S$ [40, 41]. Thus, the reduction of $D(0)$ due to the orbital order shown in Fig. 6 (a) is consistent with experimental results in Ti-oxypnictides.

IV. DISCUSSIONS

We discuss the mechanism of the superconductivity in Ti-oxypnictides. Up to now, both the spin-fluctuation-mediated unconventional pairing [29] and the phonon-mediated conventional pairing [27] mechanisms were proposed. The latter may be supported by the full-gap structure reported by the specific heat study in Ba$_{1-x}$Na$_x$Ti$_2$Sb$_2$O [42]. However, it is naturally expected that the orbital fluctuations near the orthorhombic phase would contribute to the pairing mechanism [43]. This is our important future problem.

In the present AL-VC theory, the obtained wavevector of the orbital order is $q = (0, 0, 0)$, which is consistent with the report in Ref. [24]. On the other hand, the SC-VC theory explain the incommensurate orbital order at $q_c = (\delta, 0, 0)$ in cuprate superconductors [12, 13]; $q_c$ is equal to the wavevector connecting the neighboring hot spots. This fact indicates that the incommensurate orbital order might be realized in some Ti-oxypnictides, depending on the details of the bandstructure.

In Ref. [24], the authors discussed the nematic charge order driven by the nearest-neighbor Coulomb interaction $V$. At present, there is no first principles study
for $V$. However, if $V$ were the origin of the nematic order, fine tuning of the parameters $V$ and $U$ is required to explain the development of spin fluctuations near $T_S$ in BaTi$_2$Sb$_2$O$_3$ [22]. On the other hand, the coexistence of spin and orbital fluctuations is naturally explained by the strong orbital-spin interplay described by the AL-VC. The AL-VC mechanism explains the orbital-order in Fe-based superconductors [8] and the nemtic CDW order in cuprate superconductors [12]. We stress that the importance of the AL-VC has been confirmed by the unbiased numerical study using the functional-renormalization-group theory [13, 44].

In summary, we studied the origin of the nematic order without magnetization in Ti-oxypnictides based on the three-dimensional first-principles model. We predicted the formation of the intra-unit-cell orbital order in BaTi$_2$(As,Sb)$_2$O$_3$, which is driven by the orbital-spin interplay (AL-VC). The present intra-unit-cell orbital order can be confirmed experimentally by observing the shear modulus $C_S$ and the electron Raman spectroscopy for $Bi_2$ channel, both of which are useful to observe the nematic fluctuations in Fe-based superconductors [31]. The orbital order due to the AL-VC mechanism is expected to emerge not only in the two-dimensional high-$T_c$ superconductors, but also in the three-dimensional multiorbital systems with moderate spin fluctuations such as Ti-oxypnictides. It would be an interesting future problem to clarify the role of the orbital fluctuations on the superconductivity.

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Appendix A: Numerical study of the AL-VC in three-dimensional systems

In the main text, we study the Aslamazov-Larkin vertex correction (AL-VC) in the three-dimensional 10-orbital Hubbard model for Ti-oxypnictides. To our knowledge, this is the first numerical study of the AL-VC in the three-dimensional multiorbital model.

In this model, we verified that the AL-VCs $X_{l,m,m'}^{c}(q)$ with $l \neq l'$ or $m \neq m'$ are negligibly small. Therefore, we calculate the AL-VC $X_{l,m}^{c}(q) = X_{l,l,m,m}(q)$ in the present study. Its expression is given as

$$X_{l,m}^{c}(q) = \frac{T}{2} \sum_{p} \sum_{i_1, i_2} \left\{ \Lambda_{ll,12,j1,j2}(q;p) \Lambda_{mm,13,j3,j4}(q;p) \right\} \times \left\{ 3V_{s}^{c} + V_{c}^{s} \right\}, \quad \text{(A1)}$$

where the three-point vertex and spin (charge) channel interaction are given as

$$\Lambda_{ll,12,j1,j2}(q;p) = -T \sum_{k} G_{l,i_1}(k+q)G_{j_1}(k)G_{l,i_2,j_2}(k-p), \quad \text{(A2)}$$

$$\Lambda_{mm,13,j3,j4}(q;p) = \Lambda_{j1,j4,m1,j4}(q;p) + \Lambda_{j3,j4,m1,j4}(q;-p-q), \quad \text{(A3)}$$

The diagrammatic expression of the AL-VC is shown in Fig. 7. Here, the second-order double counting terms in the AL-VC should be subtracted. In the present numerical study, we put $i_3 = i_2$, $i_4 = i_3$, $j_1 = j_2$ and $j_3 = j_4$ in eq. (A1). This simplification is justified since $\chi_{l,l',m,m}(q)$ is negligibly small for $l \neq l'$ or $m \neq m'$.

FIG. 7: The diagram of AL-VC. $X_{l,m}^{c}(q) = X_{l,l,m,m}(q)$

In general, the AL-VC is less important in higher-dimensional systems, so it is significant to verify whether orbital fluctuations due to the AL-VC could develop in three-dimensional systems. In the presence of strong spin fluctuations, the AL-VC is scaled as

$$X^c(0) \sim |\Lambda(0; Q_s)|^2 T \sum_p |V_s^c(p,0)|^2, \quad \text{(A5)}$$

which is proportional to $|\Lambda(0; Q_s)|^2 T \xi_{AF}^{-d}$ when the spin fluctuations are $d$-dimensional, where $\xi_{AF}$ is the antiferromagnetic correlation length. Therefore, the AL-VC is expected to be less important in the three-dimensional systems. Nonetheless, as revealed by the numerical study in the main text, the strong orbital fluctuations due to the AL-VC is realized in Ti-oxypnictides with three-dimensional FSs.

Appendix B: Mathematical explanation for the intra-unit-cell orbital order due to the AL-VC

In the main text, we obtained the “intra-unit-cell orbital order” based on the BaTi$_2$(As,Sb)$_2$O model, by tak-
The maximum eigenvalue of $\hat{C}_2$ gives the charge Stoner factor $\alpha_C$, and its eigenvector gives the form factor $\gamma$ at $\alpha_C = 1$. (Note that $\hat{C}_2$ is not Hermitian.) For simplicity, we examine the case of $\Phi^{(c)}_{i,m} = 0$ for $l \neq m$, and $U' = U$ and $J = 0$. In this case, the charge Stoner factor is $\alpha_C = \frac{U}{4} \left( \Phi^{(c)}_{1,1} + \Phi^{(c)}_{2,2} \right) \sqrt{\Phi^{(c)}_{1,1} + \Phi^{(c)}_{2,2} + 14\Phi^{(c)}_{2,2}} \geq 0$, and the form factor is $\gamma \propto -\Phi^{(c)}_{1,1} + \Phi^{(c)}_{2,2} + \Phi^{(c)}_{1,1}^2 + \Phi^{(c)}_{2,2}^2 + 14\Phi^{(c)}_{2,2} + 4\Phi^{(c)}_{2,2}$. When $\Phi^{(c)}_{2,2} = (1-x)\Phi^{(c)}_{1,1}$ and $|\gamma| \approx 1$, the form factor is simplified as $\gamma \propto (y, -1)$, where $y = (\sqrt{1-x} + x^2/16 - x^4)/(1-x) \approx 1 + x^4$.

For the $4 \times 4$ charge susceptibility in Eq. (B1), the charge Stoner factor and the form factor are respectively given by the maximum eigenvalue and its eigenvector of the following $4 \times 4$ matrix:

$$\hat{C}_4 = \begin{pmatrix} \hat{C} \hat{C}^\dagger \end{pmatrix}.$$  

$$\hat{C}'_2 = \begin{pmatrix} \Phi^{(c)}_{1,3} & \Phi^{(c)}_{1,4} \\ \Phi^{(c)}_{2,3} & \Phi^{(c)}_{2,4} \end{pmatrix} \begin{pmatrix} -U & -2U' + J \\ -2U' + J & -U \end{pmatrix},$$  

$$\hat{C}'_2 = \begin{pmatrix} \Phi^{(c)}_{3,1} & \Phi^{(c)}_{4,1} \\ \Phi^{(c)}_{3,2} & \Phi^{(c)}_{4,2} \end{pmatrix} \begin{pmatrix} -U & -2U' + J \\ -2U' + J & -U \end{pmatrix}.$$  

At $q = 0$, the relation $\hat{C}'_2 = \hat{C}'_2^\dagger$ holds, and the form factors are $(q, \pm g)$ when $\hat{C}'_2 = 0$. This degeneracy of the form factor is lifted in the presence of small $\hat{C}_2'$, and the form factor is given as $f \approx (g, -g)$ when the inner product $(g, \hat{C}'_2 g)$ is negative, which is satisfied in the present numerical study due to the large negative $X_{1,1;3,3}(0)$ in Table I.

To summarize, we presented a mathematical explanation why the orbital-order with the form factor $f \sim (1, -1, -1, 1)$, which corresponds to the numerical results in Figs. 4 (a) and (c), is universally obtained in the present numerical study.

Next, we analyze the intra-site spin susceptibility with $l, m \leq 2$ by neglecting the inter-site $\Phi^{(c)}_{i,m}$ ($l \leq 2, m \geq 3$). The $2 \times 2$ spin susceptibility is given as

$$\left( \begin{array}{cc} \chi^{(c)}_{1,1} & \chi^{(c)}_{1,2} \\ \chi^{(c)}_{2,1} & \chi^{(c)}_{2,2} \end{array} \right) = (1 - \hat{C}_2)^{-1} \left( \begin{array}{cc} \Phi^{(c)}_{1,1} & \Phi^{(c)}_{1,2} \\ \Phi^{(c)}_{2,1} & \Phi^{(c)}_{2,2} \end{array} \right),$$  

$$\hat{S}_2 = \begin{pmatrix} \Phi^{(c)}_{1,1} & \Phi^{(c)}_{1,2} \\ \Phi^{(c)}_{2,1} & \Phi^{(c)}_{2,2} \end{pmatrix} \begin{pmatrix} U & J \\ J & U \end{pmatrix}^{-1}.$$  

where $\Phi^{(c)}_{i,m}(q) \approx \chi^{(c)}_{i,m}(q)$ is satisfied since the AL-VC for the spin channel is small. Since $J \ll U$, only the orbital diagonal elements of the spin susceptibility $\chi^{(c)}_{i,m}$ are enlarged. The spin Stoner factor is obtained as $\alpha_s = \frac{1}{4} \left( \Phi^{(c)}_{1,1} + \Phi^{(c)}_{2,2} \right) \left( \Phi^{(c)}_{1,1}^2 + \Phi^{(c)}_{2,2}^2 + 14\Phi^{(c)}_{2,2} + 4\Phi^{(c)}_{2,2} \right)$, when $\Phi^{(c)}_{i,m}$ with $l \neq m$ is negligible.

In the RPA or FLEX approximation ($\Phi^* = \Phi'$), the relation $\alpha_C \leq \alpha_s$ holds at any $q$ for $J \geq 0$, according

| $X^0_{l,m,m}$ | $m = 1$ | 2 | 3 | 4 |
|----------------|--------|---|---|---|
| $l = 1$       | 0.364  | -0.037 | -0.034 | 0.094 |
| 2             | 0.258  | 0.094 | -0.046 |   |
| 3             | 0.364  | -0.037 |   |   |
| 4             |       | 0.258 |   |   |

| $X^c_{l,m,m}$ | $m = 1$ | 2 | 3 | 4 |
|----------------|--------|---|---|---|
| $l = 1$       | 0.844  | 0.020 | -0.252 | 0.013 |
| 2             | 0.487  | 0.013 | 0.099 |   |
| 3             | 0.844  | 0.020 |   |   |
| 4             |       | 0.487 |   |   |
to the obtained expressions for $\alpha_C$ and $\alpha_S$. Nonetheless, the opposite relation $\alpha_C > \alpha_S$ is obtained in the present study thanks to the charge channel AL-VC. Therefore, the “orbital order without magnetization” is explained by the present orbital-spin fluctuation theory with including the AL-VC.

**Appendix C: Fermi surface deformation due to intra-unit-cell orders**

(a) no order

(b) orbital order

(c) charge order

Here, we examine the orbital character of the FSs in detail, and discuss the FS deformation under the orbital and charge orders. Figure 8 (a) shows the FSs of the original tight-binding model in the $k_z = 0$ plane. The weights of the 1,3-orbitals (2,4-orbitals) are shown in the upper (lower) Brillouin zone.

First, we calculate the FS deformation under the intra-unit-cell orbital order, by introducing the potential $\Delta E_{\text{orbital}} \equiv (\Delta E, -\Delta E, -\Delta E, \Delta E)$. Figure 8 (b) shows the FSs for $\Delta E = 0.1$ eV and 0.2 eV. In this case, the hole-FS around the X-point, which is mainly composed of the 3-orbital (green), disappears for $\Delta E \geq 0.1$ eV. In addition, the electron-FS around the M-point, mainly composed by (1+4)-orbital [(2+3)-orbital] near the $k_x = \pi$ [$k_y = \pi$] Brillouin zone boundary, disappears for $\Delta E \geq 0.2$ eV. For this reason, the pseudo-gap structure appears in the DOS at the Fermi level, as shown in Fig. 5 (a) in the main text.

Next, we calculate the FS deformation under the intra-unit-cell charge order with $\Delta E_{\text{charge}} \equiv (\Delta E, \Delta E, -\Delta E, -\Delta E)$. Figure 8 (c) shows the FSs for $\Delta E = 0.1$ eV and 0.2 eV. Then, the hole-FS around the X-point disappears for $\Delta E \geq 0.1$ eV, similarly to Fig. 8 (b). However, in contrast, the electron-FS around the M-point still exists for $\Delta E = 0.2$ eV, since the potential on the (1+4)-orbital and that on the (2+3)-orbital cancel in the case of the charge order. For this reason, the pseudo-gap structure is insensitive to $\Delta E$, as shown in Fig. 5 (b) in the main text.

According to the ARPES study for Na$_2$Ti$_2$Sb$_2$O, the pseudo-gap appears around the X-point [40]. This result is consistent with the FS deformation due to orbital order in Fig. 8 (b) as well as that due to the charge order in Fig. 8 (c). To distinguish between the orbital order and charge order, the ARPES study around the M-point is required.

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