Efficient Method for Prediction of Metastable or Ground Multipolar Ordered States and Its Application in Monolayer α-RuX_3 (X = Cl, I)

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Exotic high-rank multipolar order parameters have been found to be unexpectedly active in more and more correlated materials in recent years. Such multipoles are usually dubbed "hidden orders" since they are insensitive to common experimental probes. Theoretically, it is also difficult to predict multipolar orders via *ab initio* calculations in real materials. Here, we present an efficient method to predict possible multipoles in materials based on linear response theory under random phase approximation. Using this method, we successfully predict two pure metastable magnetic octupolar states in monolayer α-$RuCl_3$, which is confirmed by self-consistent unrestricted Hartree-Fock calculations. We then demonstrate that these octupolar states can be stabilized in monolayer α-RuI_3, one of which becomes the octupolar ground state. Furthermore, we also predict a fingerprint of an orthogonal magnetization pattern produced by the octupole moment that can be easily detected by experiment. The method and the example presented in this Letter serve as a guide for searching multipolar order parameters in other correlated materials.

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Introduction.—High-rank multipolar order parameters (OPs), induced by multiple orbital degrees of freedom themselves or their coupling to spin sector via strong spin-orbital coupling (SOC), have been found to be unexpectedly active in more and more correlated materials such as $4f$, $5f$, and $5d$ systems in recent years [1–19], although they are usually considered as weak terms comparing to dipoles under multipole expansion. In some cases, they can even act as the primary OPs. One such example is the famous "hidden order" (HO) phase transition occurring around 17.5 K in URu_2Si_2 [20–29], and many different kinds of multipolar moments, including quadrupoles [30–32], octupoles [33,34], hexadecapoles [35–38], and dotriacontapoles [8,39,40], have been suggested as the primary OPs in this HO phase. Different from conventional dipoles, much richer and exotic orders and low-energy excitations can be expected to arise from multipolar OPs due to their higher degrees of freedom. For instance, superconductivity mediated by multipole fluctuation [21,40–51], multipolar Kondo effects [35,52–58] with exotic non-Fermi-liquid fixed points [58], and cross-correlated responses [11,13,59–80] have been found. Therefore, the important roles played by multipolar OPs are attracting extensive attention and are considered to be significant factors to interpret some exotic physical phenomena [4,5,9,15].

However, such high-rank OPs pose a big challenge to experimental detection since they are not coupled or are weakly coupled to the common experimental probes [81], or they are usually accompanied with a primary dipolar OP [81–85] that dominates the experimental signals. This is the reason why the multipolar OPs are usually dubbed as HOs and their roles are rarely recognized even though they might be widely present in materials. Theoretically, predicting multipolar OPs in real materials from *ab initio* calculations [8,12,22,23,35,39,86–99] is a crucial task but also not an easy one since (1) most of these materials involve both strong SOC and electronic correlations that should be properly treated by methods such as the self-consistent unrestricted Hartree-Fock mean-field (HFMF) method with all the off-diagonal terms of local density matrix kept [100]; (2) self-consistent calculations of the multipolar states depend extremely on the transcendental knowledge of the possible multipoles and the related symmetry breaking of Hamiltonian to induce the desired OPs; (3) the energy differences between different multipoles are usually very tiny. As a result, such calculations should be performed many times with very high numerical accuracy such that they take too much time and even become unfeasible in systems with many atoms. Thus, a highly efficient method to search for all the possible multipolar states is very desirable, and the predictions of their fingerprints in physical observables that can be easily measured experimentally are also very important to uncover HO physics in materials.

In this Letter, based on linear response theory (LRT) under random phase approximation (RPA) [3,8,12,40,46,49,101], we develop a numerical method starting from the density functional theory (DFT) calculations to search for all possible multipolar OPs efficiently for the spin-orbital entangled correlated electronic materials that only requires a fast single-shot calculation. We use monolayer α-RuX_3 (X = Cl, I) as an example to demonstrate its formalism, capabilities, and effectiveness. It has correctly reproduced the Zigzag magnetic ground state of α-$RuCl_3$ as found in the neutron scattering experiments [102–105], which validates our method. More importantly, two pure metastable magnetic octupolar states, O_{21}^{36}, (with ferromagnetic (FM) and antiferromagnetic (AFM) configurations, respectively) without any magnetic dipoles are predicted. These two octupolar states can be stabilized by doping I elements in α-$RuCl_3$ or synthesizing α-RuI_3 directly, where the AFM octupolar state becomes the ground state. We propose that an orthogonal magnetization $\propto H^2\cos^2\theta$ can be detected as the fingerprint of the metastable FM octupolar state [26,27,85].

Method.—In many 4*d* and 5*d* transition metal materials, the strong cubic crystal field splits the fivefold *d* orbitals into twofold e_g and threefold t_{2g} orbitals with electrons occupying only the low-energy t_{2g} subspace, so a t_{2g} model is sufficient for such systems [9,106–110]. For a t_{2g} system, the local on-site Coulomb interaction can be well described by a multiorbital Kanamori Hamiltonian [111], $H_{\rm int}$. Under HFMF approximation, we can further express $H_{\rm int}$ in terms of all the multipolar OPs in the t_{2g} subspace as follows (see the Supplemental Material [112] for details):

$$\begin{aligned} H_{\rm int}^{\rm MF} &= (5U-10J)\langle O_{00}^{01}\rangle O_{00}^{01} + (3J-U)\sum_{M=1}^{3}\langle O_{10}^{1M}\rangle O_{10}^{1M} + (5J-U)\sum_{M=1}^{5}\langle O_{20}^{2M}\rangle O_{20}^{2M} - (2J+U)\sum_{M=1}^{3}\langle O_{01}^{1M}\rangle O_{01}^{1M} \\ &+ (3J-U)\left\{\langle O_{11}^{01}\rangle O_{11}^{01} + \sum_{M=1}^{3}\langle O_{11}^{1M}\rangle O_{11}^{1M} + \sum_{M=1}^{5}\langle O_{11}^{2M}\rangle O_{11}^{2M}\right\} \\ &+ (J-U)\left\{\sum_{M=1}^{3}\langle O_{21}^{1M}\rangle O_{21}^{1M} + \sum_{M=1}^{5}\langle O_{21}^{2M}\rangle O_{21}^{2M} + \sum_{M=1}^{7}\langle O_{21}^{3M}\rangle O_{21}^{3M}\right\}, \end{aligned} \tag{1}$$

where U and J are the Coulomb interaction and Hund's coupling, respectively. $O_{K_oK_s}^{KM}$ are the 36 spin-orbital entangled multipoles with overall rank K ($K = 0 \sim 3$ and $M = 1, 2, \ldots, 2K+1$), which are composed of orbital and spin multipoles with rank K_o and K_s [100]. O_{00}^{01} and O_{11}^{01} describe the charge and isotropic SOC terms, respectively. The electric quadrupoles O_{20}^{2M} describe possible crystal field splitting in t_{2g} subspace and O_{11}^{2M} describe the corresponding anisotropic SOC effects. O_{10}^{1M} and O_{01}^{1M} are the conventional orbital and spin magnetic dipoles, and O_{21}^{3M} describe magnetic octupoles. All the potentially ordered multipoles are contained in Eq. (1), from which we can intuitively capture their explicit physical implications.

Based on Eq. (1) and the DFT constructed noninteracting Hamiltonian H_0, we use the LRT under RPA to determine which multipoles may actually occur. The flow diagram of our method is shown as Fig. 1, in which self-consistent HFMF calculations are not needed. The basic formula of LRT can be written as

$$\delta\langle O_l(\boldsymbol{q},\omega)\rangle = \sum_{l'}\chi_{ll'}(\boldsymbol{q},\omega)F_{l'}^{\rm ext}(\boldsymbol{q},\omega), \tag{2}$$

where $F_{l'}^{\rm ext}(\boldsymbol{q},\omega)$ is an external field coupled to a multipole $O_{l'}$, and $\chi_{ll'} \propto \langle[O_l, O_{l'}]\rangle_{\boldsymbol{q},\omega}$ is the interacting response function between multipoles O_l and $O_{l'}$. Under RPA, the local interactions in Eq. (1) enter into χ only via a coefficient matrix A composed of U and J (see the derivations in [112]),

$$\chi = (I - \chi^0 A)^{-1}\chi^0, \tag{3}$$

where χ^0 is the noninteracting response function obtained from the noninteracting Hamiltonian H_0, whose matrix element $\chi_{ll'}^0$ is given by [112]

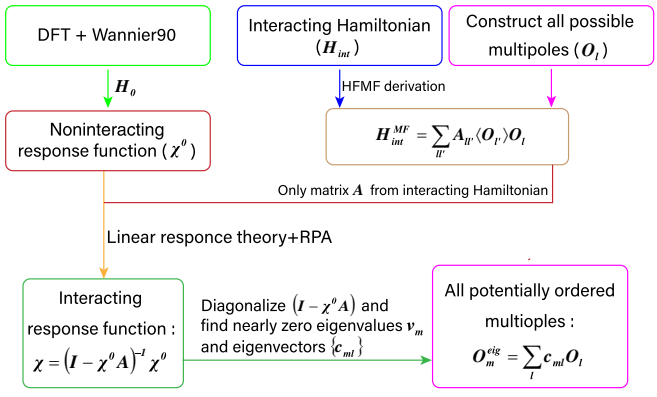

FIG. 1. Flow diagram of predicting multipolar OPs based on DFT calculations and linear response theory with RPA.

$$\chi^0_{ll'}(\boldsymbol{q},\omega) = \frac{1}{\hbar N}\sum_{\alpha\beta\gamma\delta} O_l^{i_l\alpha\beta} O_{l'}^{i_{l'}\delta\gamma} \Xi^{i_l i_{l'}}_{\alpha\beta,\delta\gamma}(\boldsymbol{q},\omega), \tag{4}$$

$$\Xi^{i_l i_{l'}}_{\alpha\beta,\delta\gamma}(\boldsymbol{q},\omega) = \sum_{\boldsymbol{k}jj'} B^{j}_{i_{l'}\gamma}(\boldsymbol{k}) B^{j*}_{i_l\alpha}(\boldsymbol{k}) B^{j'}_{i_l\beta}(\boldsymbol{k}+\boldsymbol{q}) B^{j'*}_{i_{l'}\delta}(\boldsymbol{k}+\boldsymbol{q}) \times \frac{f(\varepsilon_{j\boldsymbol{k}}) - f(\varepsilon_{j'\boldsymbol{k}+\boldsymbol{q}})}{\omega - (\varepsilon_{j'\boldsymbol{k}+\boldsymbol{q}} - \varepsilon_{j\boldsymbol{k}})/\hbar + i0^+}, \tag{5}$$

where l labels the multipole O_l, α, β, γ, δ label the spin-orbital basis, j labels the Bloch band, i_l labels the sublattice where O_l resides, $B^j_{i_l\alpha}(\boldsymbol{k})$ is the (i_l,α) component of the noninteracting wave function of the jth eigenstate at momentum $\boldsymbol{k}$ with eigenvalue $\varepsilon_{j\boldsymbol{k}}$, and $f(\varepsilon_{j\boldsymbol{k}})$ is the Fermi distribution function. Since all the interacting effects only enter into A, the interacting wave functions are not required anymore and those time-consuming self-consistent HFMF calculations are avoided in our scheme, which leads to a very fast single-shot calculation.

Here, the divergence of χ is ambiguous in the original multipole representation of $\{O_l\}$ defined in Eq. (1), since the matrix $(I-\chi^0 A)$ in the denominator of Eq. (3) is not diagonal. We can transform $\{O_l\}$ to a new (dubbed "eigen order") representation $O^{\mathrm{eig}}_m = \sum_l c_{ml} O_l$ by diagonalizing $(I-\chi^0 A)$, where c_{ml} is the lth component of the mth eigenvector of $(I-\chi^0 A)$. This indicates that the actually ordered parameter is usually a symmetry allowed combination of $\{O_l\}$. Under RPA, the response matrix χ' and χ'^0 in the new eigen-order representation satisfy the same relations as Eq. (3) and can be rewritten as $\chi'_{mm'} = \nu_m^{-1}\chi'^0_{mm'}$, where ν_m is the mth eigenvalue of $(I-\chi^0 A)$. Therefore, one can find spontaneous symmetry breaking and the corresponding OPs O_l by checking the eigenvalues of ν_m that approach to zero and analyzing their eigenvectors $\{c_m\}$.

Application in monolayer α-$RuCl_3$.—Now we apply our method to search possible multipolar OPs in the monolayer α-$RuCl_3$, which crystallizes into a nearly ideal honeycomb lattice [102,104,105,116,117] with space group P-31m (No. 162), as shown in Fig. 2(a). Similar to Ir^{4+} in iridates, Ru^{3+} with d^5 configuration will lead to half-filling of $j_{\mathrm{eff}} = \frac{1}{2}$ states when SOC is considered [106,107,116,117]. All the above features make $RuCl_3$ a famous candidate of Kitaev spin liquid. Previous works on Kitaev physics in this material consider only the $j_{\mathrm{eff}} = \frac{1}{2}$ states in the low-energy model [105,108,118–124]. However, comparing to its $5d$ counterparts such as Na_2IrO_3 and Li_2IrO_3, relatively smaller SOC strength λ in $4d$ Ru^{3+} cannot effectively isolate the $j_{\mathrm{eff}} = \frac{1}{2}$ from the $j_{\mathrm{eff}} = \frac{3}{2}$ states [100] to induce a reasonable $j_{\mathrm{eff}} = \frac{1}{2}$ single-orbital model ($\lambda = 96$ meV for Ru^{3+} and about 400 meV for Ir^{4+}). Thus the multiorbital degrees of freedom that are essential for multipolar OPs still play important roles here.

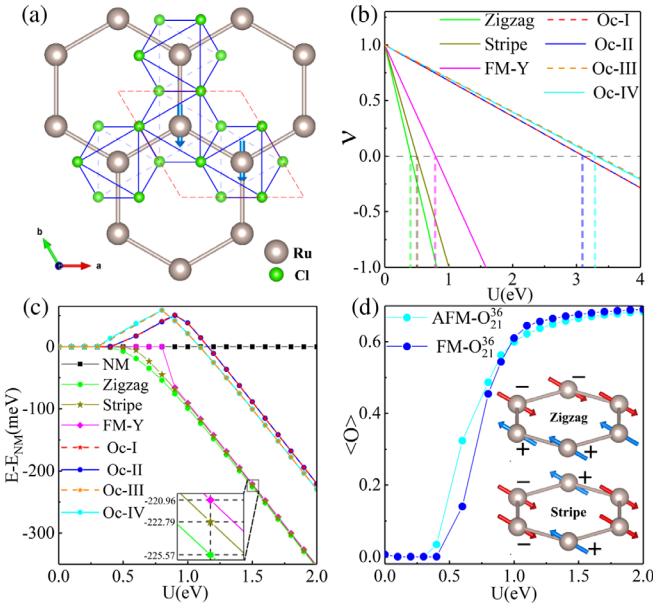

FIG. 2. (a) Crystal structure of monolayer α-$RuCl_3$. (b) The eigenvalues ν_m of $(I-\chi^0 A)$ that approach to zero as a function of U. (c) Total energy of magnetic states relative to the nonmagnetic state as a function of U. The inset shows that Zigzag magnetic order has the lowest energy. (d) The size of the O^{36}_{21} octupole moment. The insets show the "Zigzag" and "Stripe" antiferromagnetic orders, respectively. $J = 0$ eV and $\lambda = 96$ meV are used in (b)–(d).

We first construct the noninteracting t_{2g} tight-binding Hamiltonian H_0 based on the non-SOC DFT calculations by the Vienna *ab initio* simulation package (VASP) [86] combined with the maximally localized Wannier functions method [125–128]. The crystal symmetry of H_0 is restored using the code developed by Yue [129], whose band structures match well with the DFT bands [112]. An atomic SOC term of $\lambda \boldsymbol{l}\cdot\boldsymbol{s}$ with $\lambda = 96$ meV from the optical spectroscopy experiment [117] is added to H_0. The noninteracting response matrix χ_0 is calculated according to Eq. (4) using the eigen energy and wave functions of $H_0 + \lambda \boldsymbol{l}\cdot\boldsymbol{s}$. We then diagonalize $(I-\chi^0 A)$ to obtain its eigenvalues ν_m and the corresponding eigenvectors $\{c_m\}$. In Fig. 2(b), we plot ν_m that approach to zero as a function of U. The first one approaching to zero is the green curve at $U = 0.4$ eV, which corresponds to the most likely occurred order in α-$RuCl_3$. By analyzing c_{ml} as shown in the second column of Table I, we find that they are magnetic dipoles, O^{11}_{10} (O^{11}_{01}) and O^{13}_{10} (O^{13}_{01}) with $\boldsymbol{q} = [0, 0.5]$, corresponding to the Zigzag configuration [see the insert of Fig. 2(d)]. This is consistent with the neutron scattering experiment [104] and thus validates our method. The second (dark yellow) and third (pink) divergent terms correspond to the Stripe ($\boldsymbol{q} = [0, 0.5]$) and FM-Y [Fig. 2(a)] magnetic orders, respectively, which are also widely studied for α-$RuCl_3$ [130,131].

TABLE I. The predicted ordered states, $O_m^{\rm eig}=\sum_l c_{ml}O_l$, when $\nu_m\to 0$ in monolayer α-$RuCl_3$. The values in columns are the corresponding weights c_{ml} of multipoles $O_l=O^{KM}_{K_oK_s}$. $+/-$ denote the moment directions at different Ru sites, as shown in Fig. 2(d). Only the local OPs on the first Ru site are listed.

	$O_m^{\rm eig}$ (c_{ml})						
O_l	Zigzag $(++--)$	Stripe $(+--+)$	FM-Y $(++)$	Oc-I $(++)$	Oc-II $(++)$	Oc-III $(+-)$	Oc-IV $(+-)$
$O_{10}^{11}(l_x)$	−0.011	0.202	0.116	0	0	0	0
$O_{10}^{12}(l_y)$	0	0	0.065	0	0	0	0
$O_{10}^{13}(l_z)$	−0.165	−0.229	0	0.155	0	−0.147	0
$O_{01}^{11}(s_x)$	−0.058	0.121	0.594	0	0	0	0
$O_{01}^{12}(s_y)$	0	0	0.331	0	0	0	0
$O_{01}^{13}(s_z)$	−0.052	−0.140	0	−0.043	0	0.257	0
O_{21}^{33}	0	0	0	0.652	0	0.626	0
O_{21}^{36}	0	0	0	0	0.707	0	0.691

Besides these extensively studied magnetic dipolar states, we find that monolayer α-$RuCl_3$ may also enter four new magnetic octupolar states (Oc-I $\sim$ IV). As shown in Table I, the Oc-I (Oc-III) state is dominated by the FM (AFM) arranged magnetic octupole O_{21}^{33} accompanying with minor magnetic dipole components, while the Oc-II (Oc-IV) state has a pure magnetic octupole moment O_{21}^{36} with FM (AFM) arrangement. We notice that O_{21}^{33} is the counterpart of O_{21}^{36} by an operation of $x\leftrightarrow -y$, according to the original definitions [100]. Their difference is that O_{21}^{36} respects all the point group symmetries (including C_{3z} and C_{2y}) of the noninteracting Hamiltonian H_0 of monolayer α-$RuCl_3$, while O_{21}^{33} respects C_{3z} but not C_{2y} symmetry. Therefore, O_{21}^{33} can coexist with the magnetic dipoles that align along the z direction (more analyses are given in Sec. VI of [112]).

We also perform self-consistent unrestricted HFMF calculations to check the above predictions from our new method. To drive the system to a desired ordered state, we symmetrize the mean-field Hamiltonian according to its magnetic group at each step of iterations. The total energy of the converged ordered states relative to the nonmagnetic (NM) state as functions of U are plotted in Fig. 2(c), which confirms our prediction that the Zigzag antiferromagnetic ordered state is the ground state when $U>0.4$ eV, whose energy is about $2\sim 4$ meV lower than the other two magnetic dipolar states. We notice that the Oc-I $\sim$ IV states can also be stabilized by U around $0.5\sim 1.1$ eV ($J=0$ eV), although their energy is higher than the NM state. When U exceeds 1.15 eV, their energy becomes lower than the NM state. The energy difference between Oc-I (Oc-III) and Oc-II (Oc-IV) is very tiny at $J=0$ eV (Oc-II is about 10^{-4} meV lower than Oc-I). When $J\geq 0.22$ eV, the Oc-I (Oc-III) state can not be stabilized anymore [112]. Therefore, we only study the Oc-II (Oc-IV) state, i.e., the FM-O_{21}^{36} (AFM-O_{21}^{36}) state, hereafter.

The calculated size of the O_{21}^{36} octupole moments in FM- and AFM-O_{21}^{36} states with respect to U are plotted in Fig. 2(d). It shows that this octupole moment appears around $U=0.5$ eV, then increases monotonously as increasing U, and finally saturates once entering into the metastable state. These features show a typical first-order phase transition [132] from NM to the O_{21}^{36} state. All the self-consistent HFMF calculations are consistent with our predictions, which validates our new method.

We now study the electronic structures of the O_{21}^{36} states. Here, in Fig. 3(a) we plot the band structures of AFM-O_{21}^{36} state since it is more favorable in energy [about 12 meV lower than the FM-O_{21}^{36} state; see Fig. 2(c)]. The color bar in Fig. 3(a) shows the orbital projection of $j_{\rm eff}=\frac{1}{2},\frac{3}{2}$. Different from the typical band structures of a t_{2g} system with SOC, the unoccupied bands in AFM-O_{21}^{36} state are mainly the $j_{\rm eff}=\frac{3}{2}$ type rather than the $j_{\rm eff}=\frac{1}{2}$ type, which is caused by an interaction-induced positive SOC $\lambda\langle \boldsymbol{l}\cdot\boldsymbol{s}\rangle$ [see cyan curve in Fig. 3(b)]. On the contrary, the Zigzag and NM states have negative $\lambda\langle \boldsymbol{l}\cdot\boldsymbol{s}\rangle$.

In the following, we would like to discuss how to stabilize such O_{21}^{36} states in materials. First, two rotation symmetries, which can forbid the presence of dipolar OPs, are the necessary condition to protect such a pure octupole. Second, our results in Fig. 3(b) obviously demonstrate that negative SOC $(-\lambda)$ could reduce the energy of O_{21}^{36} states by $\lambda\langle \boldsymbol{l}\cdot\boldsymbol{s}\rangle$. In Fig. 3(c), we plot the energy versus λ for different magnetic states in monolayer α-$RuCl_3$ at experimental U and J, which indicates that negative λ indeed makes the energy of O_{21}^{36} states much closer to dipolar states. More interestingly, when $\lambda<-73$ meV, the AFM-O_{21}^{36} state becomes the ground state, whose energy is $\sim$1 meV lower than the Zigzag dipolar ordered state. In real materials, this can be achieved by mixing t_{2g} orbitals with more p orbitals, since $-\lambda \boldsymbol{l}_{t_{2g}}\cdot\boldsymbol{s}=\lambda(-\boldsymbol{l}_{t_{2g}})\cdot\boldsymbol{s}=\lambda\boldsymbol{l}_p\cdot\boldsymbol{s}$ [133,134]. This can be realized by doping I elements in α-$RuCl_3$ or synthesizing

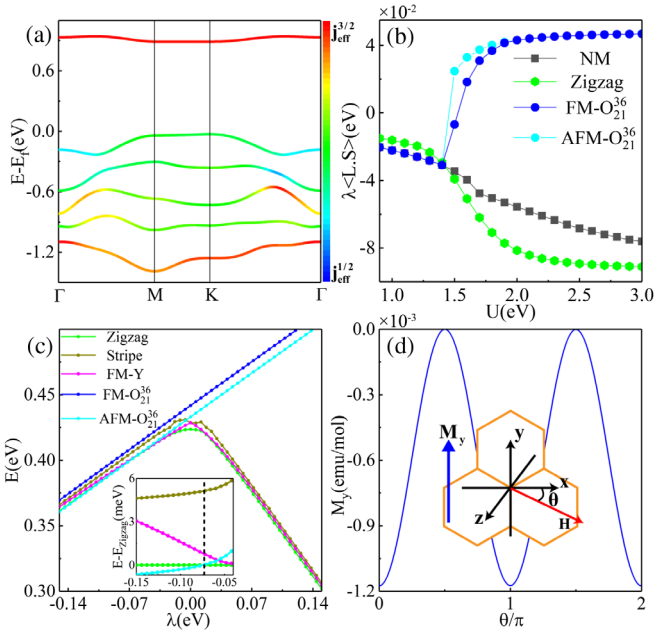

FIG. 3. (a) Band structures of the AFM-O_{21}^{36} state at the experimental $U = 2.4$ eV and $\lambda = 96$ meV. The color bar shows the orbital projection of $j_{\text{eff}} = 1/2, 3/2$. (b) Effective SOC $\lambda\langle \boldsymbol{l} \cdot \boldsymbol{s} \rangle$ of the NM, Zigzag, FM-, and AFM-O_{21}^{36} states as a function of U at $\lambda = 96$ meV. (c) Energy of magnetic states of monolayer α-$RuCl_3$ as a function of λ at $U = 2.4$ eV. (d) Orthogonal magnetic moment M_y produced by O_{21}^{36} octupole calculated at $U = 2.4$ eV and $\lambda = 96$ meV under a rotating magnetic field of 5 T applied in the xz plane. $J = 0.4$ eV is used in (a)–(d).

α-RuI_3 directly. As shown in Fig. S4 in the Supplemental Material [112], the orbital projection of the hypothetical monolayer α-RuI_3 with an optimized structure exhibits an enhancement of the $j_{\text{eff}} = 3/2$ character around the Fermi level compared to α-$RuCl_3$, which implies that a negative $\lambda \approx -100$ meV is realized. We then calculate the magnetic states of α-RuI_3 using the same method, as shown in Fig. S5 of [112], where the AFM-O_{21}^{36} state becomes the ground state with its energy about 3 meV lower than the Zigzag dipolar state.

Finally, we would like to discuss how to detect the octupolar states O_{21}^{36}. Under an external magnetic field H, the free energy contributed by O_{21}^{36} is proportional to $3H_x^2H_y - H_y^3$ [112]. Its H_y derivative gives rise to a magnetic moment in the y direction in the form of $M_y \propto H_x^2 - H_y^2$. Thus, an orthogonal magnetization oscillation of $M_y \propto H^2\cos^2\theta$ would be expected if a rotating magnetic field H is applied in the xz plane with θ respect to x axis. Figure 3(d) shows the calculated M_y of the FM-O_{21}^{36} state in monolayer α-$RuCl_3$ as a function of θ under a magnetic field of 5 T. The induced M_y is about 10^{-3} emu/mol, which is completely contributed by the octupole O_{21}^{36} since no dipole exists, in contrast to the case in $Eu_2Ir_2O_7$ [85,100]. This can be taken as a fingerprint for experimental detection of the O_{21}^{36} state. However, no orthogonal magnetization could be detected in the AFM-O_{21}^{36} state since the induced M_y on two Ru^{3+} cancel out. How to detect the AFM-O_{21}^{36} state is an open question and requires further study.

Conclusion.—In summary, we have presented an efficient method to predict metastable and ground multipolar states in real materials, in which both electronic correlation and SOC play important roles. We apply this method to study α-RuX_3 (X = Cl, I). It has not only correctly reproduced the magnetic ground state observed in experiments but also successfully predicted two metastable magnetic octupolar states in α-$RuCl_3$, which are confirmed by further self-consistent unrestricted HFMF calculations. We show that these metastable magnetic octupolar states can be stabilized and the AFM-O_{21}^{36} even becomes the ground state in α-RuI_3 via mixing t_{2g} orbitals with more p components. We also predict that an orthogonal magnetization M_y can arise from the FM-O_{21}^{36} state, which is the fingerprint and can be easily detected by magnetic torque experiment [26,27,85]. Our scheme serves as a guidance for the efficient prediction and realization of metastable and ground multipolar states in d-orbital systems.

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[1] Y. Tokunaga, D. Aoki, Y. Homma, S. Kambe, H. Sakai, S. Ikeda, T. Fujimoto, R. E. Walstedt, H. Yasuoka, E. Yamamoto, A. Nakamura, and Y. Shiokawa, Phys. Rev. Lett. **97**, 257601 (2006).
[2] Y. Tokunaga, Y. Homma, S. Kambe, D. Aoki, K. Ikushima, H. Sakai, S. Ikeda, E. Yamamoto, A. Nakamura, Y. Shiokawa, T. Fujimoto, R. E. Walstedt, and H. Yasuoka, J. Phys. Soc. Jpn. **75**, 33 (2006).
[3] H. Kusunose, J. Phys. Soc. Jpn. **77**, 064710 (2008).
[4] P. Santini, S. Carretta, G. Amoretti, R. Caciuffo, N. Magnani, and G. H. Lander, Rev. Mod. Phys. **81**, 807 (2009).
[5] Y. Kuramoto, H. Kusunose, and A. Kiss, J. Phys. Soc. Jpn. **78**, 072001 (2009).
[6] G. Chen, R. Pereira, and L. Balents, Phys. Rev. B **82**, 174440 (2010).

[7] G. Chen and L. Balents, Phys. Rev. B **84**, 094420 (2011).
[8] H. Ikeda, M.-T. Suzuki, R. Arita, T. Takimoto, T. Shibauchi, and Y. Matsuda, Nat. Phys. **8**, 528 (2012).
[9] W. Witczak-Krempa, G. Chen, Y. B. Kim, and L. Balents, Annu. Rev. Condens. Matter Phys. **5**, 57 (2014).
[10] J. W. Harter, Z. Y. Zhao, J.-Q. Yan, D. G. Mandrus, and D. Hsieh, Science **356**, 295 (2017).
[11] M.-T. Suzuki, T. Koretsune, M. Ochi, and R. Arita, Phys. Rev. B **95**, 094406 (2017).
[12] M.-T. Suzuki, H. Ikeda, and P. M. Oppeneer, J. Phys. Soc. Jpn. **87**, 041008 (2018).
[13] S. Hayami and H. Kusunose, J. Phys. Soc. Jpn. **87**, 033709 (2018).
[14] S. Hayami, M. Yatsushiro, Y. Yanagi, and H. Kusunose, Phys. Rev. B **98**, 165110 (2018).
[15] H. Watanabe and Y. Yanase, Phys. Rev. B **98**, 245129 (2018).
[16] H. Ishikawa, T. Takayama, R. K. Kremer, J. Nuss, R. Dinnebier, K. Kitagawa, K. Ishii, and H. Takagi, Phys. Rev. B **100**, 045142 (2019).
[17] D. D. Maharaj, G. Sala, M. B. Stone, E. Kermarrec, C. Ritter, F. Fauth, C. A. Marjerrison, J. E. Greedan, A. Paramekanti, and B. D. Gaulin, Phys. Rev. Lett. **124**, 087206 (2020).
[18] A. Paramekanti, D. D. Maharaj, and B. D. Gaulin, Phys. Rev. B **101**, 054439 (2020).
[19] D. Hirai, H. Sagayama, S. Gao, H. Ohsumi, G. Chen, T.-h. Arima, and Z. Hiroi, Phys. Rev. Research **2**, 022063(R) (2020).
[20] T. T. M. Palstra, A. A. Menovsky, J. van den Berg, A. J. Dirkmaat, P. H. Kes, G. J. Nieuwenhuys, and J. A. Mydosh, Phys. Rev. Lett. **55**, 2727 (1985).
[21] H. Ikeda and Y. Ohashi, Phys. Rev. Lett. **81**, 3723 (1998).
[22] S. Elgazzar, J. Rusz, M. Amft, P. M. Oppeneer, and J. A. Mydosh, Nat. Mater. **8**, 337 (2009).
[23] P. M. Oppeneer, J. Rusz, S. Elgazzar, M.-T. Suzuki, T. Durakiewicz, and J. A. Mydosh, Phys. Rev. B **82**, 205103 (2010).
[24] J. A. Mydosh and P. M. Oppeneer, Rev. Mod. Phys. **83**, 1301 (2011).
[25] P. M. Oppeneer, S. Elgazzar, J. Rusz, Q. Feng, T. Durakiewicz, and J. A. Mydosh, Phys. Rev. B **84**, 241102(R) (2011).
[26] R. Okazaki, T. Shibauchi, H. J. Shi, Y. Haga, T. D. Matsuda, E. Yamamoto, Y. Onuki, H. Ikeda, and Y. Matsuda, Science **331**, 439 (2011).
[27] S. Tonegawa, K. Hashimoto, K. Ikada, Y.-H. Lin, H. Shishido, Y. Haga, T. D. Matsuda, E. Yamamoto, Y. Onuki, H. Ikeda, Y. Matsuda, and T. Shibauchi, Phys. Rev. Lett. **109**, 036401 (2012).
[28] J.-Q. Meng, P. M. Oppeneer, J. A. Mydosh, P. S. Riseborough, K. Gofryk, J. J. Joyce, E. D. Bauer, Y. Li, and T. Durakiewicz, Phys. Rev. Lett. **111**, 127002 (2013).
[29] J. Mydosh and P. Oppeneer, Philos. Mag. **94**, 3642 (2014).
[30] P. Santini and G. Amoretti, Phys. Rev. Lett. **73**, 1027 (1994).
[31] P. Santini, Phys. Rev. B **57**, 5191 (1998).
[32] F. J. Ohkawa and H. Shimizu, J. Phys. Condens. Matter **11**, L519 (1999).
[33] A. Kiss and P. Fazekas, Phys. Rev. B **71**, 054415 (2005).
[34] K. Hanzawa, J. Phys. Condens. Matter **19**, 072202 (2007).
[35] K. Haule and G. Kotliar, Nat. Phys. **5**, 796 (2009).
[36] H. Kusunose and H. Harima, J. Phys. Soc. Jpn. **80**, 084702 (2011).
[37] H.-H. Kung, R. E. Baumbach, E. D. Bauer, V. K. Thorsmølle, W.-L. Zhang, K. Haule, J. A. Mydosh, and G. Blumberg, Science **347**, 1339 (2015).
[38] H.-H. Kung, S. Ran, N. Kanchanavatee, V. Krapivin, A. Lee, J. A. Mydosh, K. Haule, M. B. Maple, and G. Blumberg, Phys. Rev. Lett. **117**, 227601 (2016).
[39] F. Cricchio, F. Bultmark, O. Grånäs, and L. Nordström, Phys. Rev. Lett. **103**, 107202 (2009).
[40] H. Ikeda, M.-T. Suzuki, R. Arita, and T. Takimoto, C. R. Phys. **15**, 587 (2014), emergent phenomena in actinides.
[41] H. Kotegawa, M. Yogi, Y. Imamura, Y. Kawasaki, G.-q. Zheng, Y. Kitaoka, S. Ohsaki, H. Sugawara, Y. Aoki, and H. Sato, Phys. Rev. Lett. **90**, 027001 (2003).
[42] M. Koga, M. Matsumoto, and H. Shiba, J. Phys. Soc. Jpn. **75**, 014709 (2006).
[43] T. Goto, R. Kurihara, K. Araki, K. Mitsumoto, M. Akatsu, Y. Nemoto, S. Tatematsu, and M. Sato, J. Phys. Soc. Jpn. **80**, 073702 (2011).
[44] K. Matsubayashi, T. Tanaka, A. Sakai, S. Nakatsuji, Y. Kubo, and Y. Uwatoko, Phys. Rev. Lett. **109**, 187004 (2012).
[45] S. Kittaka, Y. Aoki, Y. Shimura, T. Sakakibara, S. Seiro, C. Geibel, F. Steglich, H. Ikeda, and K. Machida, Phys. Rev. Lett. **112**, 067002 (2014).
[46] H. Ikeda, M.-T. Suzuki, and R. Arita, Phys. Rev. Lett. **114**, 147003 (2015).
[47] T. Nomoto, K. Hattori, and H. Ikeda, Phys. Rev. B **94**, 174513 (2016).
[48] S. Sumita and Y. Yanase, Phys. Rev. B **93**, 224507 (2016).
[49] K. Hattori, T. Nomoto, T. Hotta, and H. Ikeda, J. Phys. Soc. Jpn. **86**, 113702 (2017).
[50] T. Yamashita *et al.*, Sci. Adv. **3**, e1601667 (2017).
[51] X. Bai, S.-S. Zhang, Z. Dun, H. Zhang, Q. Huang, H. Zhou, M. B. Stone, A. I. Kolesnikov, F. Ye, C. D. Batista, and M. Mourigal, Nat. Phys. **17**, 467 (2021).
[52] D. L. Cox, Phys. Rev. Lett. **59**, 1240 (1987).
[53] D. Cox, J. Magn. Magn. Mater. **76–77**, 53 (1988).
[54] A. Yatskar, W. P. Beyermann, R. Movshovich, and P. C. Canfield, Phys. Rev. Lett. **77**, 3637 (1996).
[55] D. L. Cox and A. Zawadowski, Adv. Phys. **47**, 599 (1998).
[56] T. Onimaru and H. Kusunose, J. Phys. Soc. Jpn. **85**, 082002 (2016).
[57] Y. Yamane, T. Onimaru, K. Wakiya, K. T. Matsumoto, K. Umeo, and T. Takabatake, Phys. Rev. Lett. **121**, 077206 (2018).
[58] A. S. Patri and Y. B. Kim, Phys. Rev. X **10**, 041021 (2020).
[59] Y. F. Popov, A. M. Kadomtseva, D. V. Belov, G. P. Vorobv, and A. K. Zvezdin, JETP Lett. **69**, 330 (1999).
[60] N. Hur, S. Park, P. A. Sharma, S. Guha, and S.-W. Cheong, Phys. Rev. Lett. **93**, 107207 (2004).
[61] B. Lorenz, Y. Q. Wang, Y. Y. Sun, and C. W. Chu, Phys. Rev. B **70**, 212412 (2004).
[62] R. C. Rai, J. Cao, J. L. Musfeldt, S. B. Kim, S.-W. Cheong, and X. Wei, Phys. Rev. B **75**, 184414 (2007).

[63] S. Chikara, O. Korneta, W. P. Crummett, L. E. DeLong, P. Schlottmann, and G. Cao, Phys. Rev. B **80**, 140407(R) (2009).

[64] S. Hayami, H. Kusunose, and Y. Motome, Phys. Rev. B **90**, 024432 (2014).

[65] S. Hayami, H. Kusunose, and Y. Motome, Phys. Rev. B **90**, 081115(R) (2014).

[66] S. Hayami, H. Kusunose, and Y. Motome, J. Phys. Conf. Ser. **592**, 012101 (2015).

[67] S. Hayami, H. Kusunose, and Y. Motome, J. Phys. Soc. Jpn. **84**, 064717 (2015).

[68] S. Hayami, H. Kusunose, and Y. Motome, J. Phys. Conf. Ser. **592**, 012131 (2015).

[69] N. D. Khanh, N. Abe, H. Sagayama, A. Nakao, T. Hanashima, R. Kiyanagi, Y. Tokunaga, and T. Arima, Phys. Rev. B **93**, 075117 (2016).

[70] S. Hayami, H. Kusunose, and Y. Motome, J. Phys. Condens. Matter **28**, 395601 (2016).

[71] S. Hayami, H. Kusunose, and Y. Motome, J. Phys. Soc. Jpn. **85**, 053705 (2016).

[72] M. Matsumoto, K. Chimata, and M. Koga, J. Phys. Soc. Jpn. **86**, 034704 (2017).

[73] Y. Yanagi and H. Kusunose, J. Phys. Soc. Jpn. **86**, 083703 (2017).

[74] M. Ikhlas, T. Tomita, T. Koretsune, M.-T. Suzuki, D. Nishio-Hamane, R. Arita, Y. Otani, and S. Nakatsuji, Nat. Phys. **13**, 1085 (2017).

[75] S. Hayami, H. Kusunose, and Y. Motome, Phys. Rev. B **97**, 024414 (2018).

[76] S. Hayami, H. Kusunose, and Y. Motome, Physica (Amsterdam) **536B**, 649 (2018).

[77] Y. Yanagi, S. Hayami, and H. Kusunose, Physica (Amsterdam) **536B**, 107 (2018).

[78] Y. Yanagi, S. Hayami, and H. Kusunose, Phys. Rev. B **97**, 020404(R) (2018).

[79] F. Thöle and N. A. Spaldin, Phil. Trans. R. Soc. A **376**, 20170450 (2018).

[80] A. Shitade, H. Watanabe, and Y. Yanase, Phys. Rev. B **98**, 020407(R) (2018).

[81] Y. L. Wang, G. Fabbris, D. Meyers, N. H. Sung, R. E. Baumbach, E. D. Bauer, P. J. Ryan, J.-W. Kim, X. Liu, M. P. M. Dean, G. Kotliar, and X. Dai, Phys. Rev. B **96**, 085146 (2017).

[82] H. Amitsuka, T. Inami, M. Yokoyama, S. Takayama, Y. Ikeda, I. Kawasaki, Y. Homma, H. Hidaka, and T. Yanagisawa, J. Phys. Conf. Ser. **200**, 012007 (2010).

[83] H. C. Walker, R. Caciuffo, D. Aoki, F. Bourdarot, G. H. Lander, and J. Flouquet, Phys. Rev. B **83**, 193102 (2011).

[84] R. D. dos Reis, L. S. I. Veiga, D. Haskel, J. C. Lang, Y. Joly, F. G. Gandra, and N. M. Souza-Neto, arXiv: 1601.02443.

[85] T. Liang, T. Hsieh, J. Ishikawa, S. Nakatsuji, L. Fu, and N. Ong, Nat. Phys. **13**, 599 (2017).

[86] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).

[87] D. B. Ghosh, S. K. De, P. M. Oppeneer, and M. S. S. Brooks, Phys. Rev. B **72**, 115123 (2005).

[88] A. B. Shick, V. Janiš, and P. M. Oppeneer, Phys. Rev. Lett. **94**, 016401 (2005).

[89] M.-T. Suzuki and P. M. Oppeneer, Phys. Rev. B **80**, 161103(R) (2009).

[90] M.-T. Suzuki and H. Harima, J. Phys. Soc. Jpn. **79**, 024705 (2010).

[91] M.-T. Suzuki, N. Magnani, and P. M. Oppeneer, Phys. Rev. B **82**, 241103(R) (2010).

[92] P. Söderlind, G. Kotliar, K. Haule, P. M. Oppeneer, and D. Guillaumont, MRS Bull. **35**, 883 (2010).

[93] A. Modin, Y. Yun, M.-T. Suzuki, J. Vegelius, L. Werme, J. Nordgren, P. M. Oppeneer, and S. M. Butorin, Phys. Rev. B **83**, 075113 (2011).

[94] M.-T. Suzuki, N. Magnani, and P. M. Oppeneer, Phys. Rev. B **88**, 195146 (2013).

[95] M.-T. Suzuki and H. Ikeda, Phys. Rev. B **90**, 184407 (2014).

[96] M. Werwiński, J. Rusz, J. A. Mydosh, and P. M. Oppeneer, Phys. Rev. B **90**, 064430 (2014).

[97] T. Goho and H. Harima, J. Phys. Conf. Ser. **592**, 012100 (2015).

[98] P. Maldonado, L. Paolasini, P. M. Oppeneer, T. R. Forrest, A. Prodi, N. Magnani, A. Bosak, G. H. Lander, and R. Caciuffo, Phys. Rev. B **93**, 144301 (2016).

[99] M.-T. Huebsch, T. Nomoto, M.-T. Suzuki, and R. Arita, Phys. Rev. X **11**, 011031 (2021).

[100] Y. Wang, H. Weng, L. Fu, and X. Dai, Phys. Rev. Lett. **119**, 187203 (2017).

[101] R. A. Jishi, *Feynman Diagram Techniques in Condensed Matter Physics* (Cambridge University Press, Cambridge, England, 2013).

[102] J. A. Sears, M. Songvilay, K. W. Plumb, J. P. Clancy, Y. Qiu, Y. Zhao, D. Parshall, and Y.-J. Kim, Phys. Rev. B **91**, 144420 (2015).

[103] R. D. Johnson, S. C. Williams, A. A. Haghighirad, J. Singleton, V. Zapf, P. Manuel, I. I. Mazin, Y. Li, H. O. Jeschke, R. Valentí, and R. Coldea, Phys. Rev. B **92**, 235119 (2015).

[104] H. B. Cao, A. Banerjee, J.-Q. Yan, C. A. Bridges, M. D. Lumsden, D. G. Mandrus, D. A. Tennant, B. C. Chakoumakos, and S. E. Nagler, Phys. Rev. B **93**, 134423 (2016).

[105] A. Banerjee, C. A. Bridges, J.-Q. Yan, A. A. Aczel, L. Li, M. B. Stone, G. E. Granroth, M. D. Lumsden, Y. Yiu, J. Knolle, S. Bhattacharjee, D. L. Kovrizhin, R. Moessner, D. A. Tennant, D. G. Mandrus, and S. E. Nagler, Nat. Mater. **15**, 733 (2016).

[106] B. J. Kim, H. Jin, S. J. Moon, J.-Y. Kim, B.-G. Park, C. S. Leem, J. Yu, T. W. Noh, C. Kim, S.-J. Oh, J.-H. Park, V. Durairaj, G. Cao, and E. Rotenberg, Phys. Rev. Lett. **101**, 076402 (2008).

[107] B. J. Kim, H. Ohsumi, T. Komesu, S. Sakai, T. Morita, H. Takagi, and T. Arima, Science **323**, 1329 (2009).

[108] G. Jackeli and G. Khaliullin, Phys. Rev. Lett. **102**, 017205 (2009).

[109] D. Pesin and L. Balents, Nat. Phys. **6**, 376 (2010).

[110] J. G. Rau, E. K.-H. Lee, and H.-Y. Kee, Annu. Rev. Condens. Matter Phys. **7**, 195 (2016).

[111] A. Georges, L. d. Medici, and J. Mravlje, Annu. Rev. Condens. Matter Phys. **4**, 137 (2013).

[112] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.127.147202 for the computational details, which includes Refs. [111,113–115] .

[113] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[114] R. E. Raab, *Multipole Theory in Electromagnetism: Classical, Quantum, and Symmetry Aspects, with Applications*, International Series of Monographs on Physics Vol. 128 (Clarendon Press, Oxford, 2005).
[115] P. Fazekas, *Lecture Notes on Electron Correlation and Magnetism* (World Scientific, Singapore, 1999).
[116] K. W. Plumb, J. P. Clancy, L. J. Sandilands, V. V. Shankar, Y. F. Hu, K. S. Burch, H.-Y. Kee, and Y.-J. Kim, Phys. Rev. B **90**, 041112(R) (2014).
[117] L. J. Sandilands, Y. Tian, A. A. Reijnders, H.-S. Kim, K. W. Plumb, Y.-J. Kim, H.-Y. Kee, and K. S. Burch, Phys. Rev. B **93**, 075144 (2016).
[118] J. c. v. Chaloupka, G. Jackeli, and G. Khaliullin, Phys. Rev. Lett. **105**, 027204 (2010).
[119] H.-S. Kim and H.-Y. Kee, Phys. Rev. B **93**, 155143 (2016).
[120] I. A. Leahy, C. A. Pocs, P. E. Siegfried, D. Graf, S.-H. Do, K.-Y. Choi, B. Normand, and M. Lee, Phys. Rev. Lett. **118**, 187203 (2017).
[121] S.-H. Baek, S.-H. Do, K.-Y. Choi, Y. S. Kwon, A. U. B. Wolter, S. Nishimoto, J. van den Brink, and B. Büchner, Phys. Rev. Lett. **119**, 037201 (2017).
[122] P. Lampen-Kelley, S. Rachel, J. Reuther, J.-Q. Yan, A. Banerjee, C. A. Bridges, H. B. Cao, S. E. Nagler, and D. Mandrus, Phys. Rev. B **98**, 100403(R) (2018).
[123] Y. Kasahara, T. Ohnishi, Y. Mizukami, O. Tanaka, S. Ma, K. Sugii, N. Kurita, H. Tanaka, J. Nasu, Y. Motome *et al.*, Nature (London) **559**, 227 (2018).
[124] R. Hentrich, A. U. B. Wolter, X. Zotos, W. Brenig, D. Nowak, A. Isaeva, T. Doert, A. Banerjee, P. Lampen-Kelley, D. G. Mandrus, S. E. Nagler, J. Sears, Y.-J. Kim, B. Büchner, and C. Hess, Phys. Rev. Lett. **120**, 117204 (2018).
[125] A. A. Mostofi, J. R. Yates, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, Comput. Phys. Commun. **178**, 685 (2008).
[126] J. Kuneš, R. Arita, P. Wissgott, A. Toschi, H. Ikeda, and K. Held, Comput. Phys. Commun. **181**, 1888 (2010).
[127] H. Ikeda, R. Arita, and J. Kuneš, Phys. Rev. B **81**, 054502 (2010).
[128] N. Marzari, A. A. Mostofi, J. R. Yates, I. Souza, and D. Vanderbilt, Rev. Mod. Phys. **84**, 1419 (2012).
[129] The code for symmetrization of the Wannier Hamiltonian H_0 is available on https://github.com/yuechm/Wannier_Hamiltonian_symmetrization.
[130] H.-S. Kim, V. VijayShankar, A. Catuneanu, and H.-Y. Kee, Phys. Rev. B **91**, 241110(R) (2015).
[131] Y. S. Hou, H. J. Xiang, and X. G. Gong, Phys. Rev. B **96**, 054410 (2017).
[132] D. I. Khomskii, *Basic Aspects of the Quantum Theory of Solids: Order and Elementary Excitations* (Cambridge University Press, Cambridge, England, 2010).
[133] X.-L. Sheng, Z. Wang, R. Yu, H. Weng, Z. Fang, and X. Dai, Phys. Rev. B **90**, 245308 (2014).
[134] S. Nie, G. Xu, F. B. Prinz, and S.-c. Zhang, Proc. Natl. Acad. Sci. U.S.A. **114**, 10596 (2017).