

Dynamical correlations and Mott localization in a paramagnetic VI_3 bulk crystal

Luis Craco^{1,2} and Sabrina S. Carara¹

¹*Institute of Physics, Federal University of Mato Grosso, 78060-900 Cuiabá, MT, Brazil*

²*Leibniz Institute for Solid State and Materials Research Dresden, D-01069 Dresden, Germany*



(Received 8 December 2025; revised 2 March 2026; accepted 16 March 2026; published 6 April 2026)

We perform a comprehensive study on the correlated electronic structure reconstruction of paramagnetic VI_3 crystal in its rhombohedral and monoclinic structural phases. Using density-functional plus dynamical mean-field theory (DFT + DMFT) calculations, we explicitly demonstrate the importance of local dynamical correlations for a consistent understanding of the emergent Mott state, showing the interplay between orbital-dependent one-electron line shape and multiorbital electronic interactions. Our results for the Mott gap are shown to be consistent with extant theory and experimental studies on nonmagnetic VI_3 bulk crystal. We also explore the changes in the strongly correlated electronic state upon increasing the total V band filling of monoclinic VI_3 , showing the robustness of Mott localization against electron doping. Our correlated many-body study is relevant to understanding the electronic structure reconstruction of paramagnetic vanadium-contained trihalide crystals and should be widely applicable to other van der Waals magnetic materials.

DOI: [10.1103/27xw-hjqk](https://doi.org/10.1103/27xw-hjqk)

I. INTRODUCTION

The search for two-dimensional (2D) magnetic materials for spintronic applications has emerged as a hot topic in solid-state and material physics [1]. In this context the present-day discovery of atomically thin magnetic materials with long-range order [2] has established the layered van der Waals (vdW) approach as a model system for studying magnetism in a layer-by-layer fashion. These layered magnetic crystals present a wide variety of magnetic phases, such as ferromagnets, antiferromagnets, spin liquids, multiferroics, and magnetic topological insulators [3]. However, in spite of their relevance for fundamental low-dimensional research, the role of multiorbital (MO) electronic correlations in many of these layered materials has not been examined from the bulk down to the monolayer limit. How magnetism associated with electronic correlations and structural properties are linked to one another remains an intriguing question in this emerging field. Importantly, within the vdW context, vanadium triiodide (VI_3) [4–7] is considered to be a new model system to explore 2D magnetism. This material shares intrinsic features of layered $3d$ transition-metal trihalides (MX_3 ; $M = \text{Cr}, \text{V}$; $X = \text{I}, \text{Br}, \text{Cl}$) crystals [8]: the magnetic moments are carried by the M cations coordinated by nonmagnetic halogen X ions [9]. However, VI_3 appears to differ from other layered magnets due to its combination of strong magnetic anisotropy and spin-lattice coupling effects [10].

The layer unit structure of VI_3 is described by a V cation occupying the center of three honeycomb lattice planes and

surrounded by six I anions arranged with octahedral coordination and located within the two external planes [11]. In analogy to CrI_3 , VI_3 is considered to be a member of the Ising ferromagnet family, showing long-range ferromagnetic order below 50 K with out-of-plane directed magnetic moments carried by the M atoms [6,7,12]. Upon cooling, VI_3 undergoes structural phase transitions at different temperatures [11–13]. Near room temperatures it has a hexagonal- or rhombohedral-like structure (space group $R\bar{3}$) that is reduced to a monoclinic structural ($C2m$) phase [7,13]. This phase transition is described as a change in the stacking order of the layer planes within the unit cell, which does not affect the metal-iodine bonds and the local octahedral symmetry of the I_6 cluster unit [11,14]. In VI_3 , V is in a $V^{3+}(d^2)$ valence state, yielding $S = 1$ [5,13,15], with an activation energy of 0.16 eV [5] and an optical band gap of ≈ 0.6 eV at room temperature [6].

It is worth noting that the magnetically ordered states of VI_3 have been investigated in Refs. [14–20], showing the interplay of spin magnetism, orbital magnetism, and atomic and electronic structure from bulk down to its monolayer limit. Importantly, to address the role played by electron-electron interaction, *ab initio* density-functional theories (DFT) plus Hubbard U (DFT + U) [7,15–18,21,22] and DFT plus dynamical mean-field theory (DFT + DMFT) [19,20] calculations have been performed in recent years. The DFT and DFT + U calculations correctly describe the insulating electronic state of the ferromagnetically ordered phase [15,16,19], showing spin-polarized V - $3d$ electron bands. A perusal of extant DFT + U studies, which explicitly take into account the effect of electron-electron interactions in the V $3d$ shell, reveals that the on-site Coulomb interaction U for the V_3 vdW layered family could reach values up to 4.3 eV [15]. Moreover, an on-site Coulomb interaction of $U = 6.0$ eV was also considered in a DFT + DMFT study [19] for the $R\bar{3}$ [13] structural phase. However, in spite of two earlier

Published by the American Physical Society under the terms of the Creative Commons Attribution 4.0 International license. Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI.

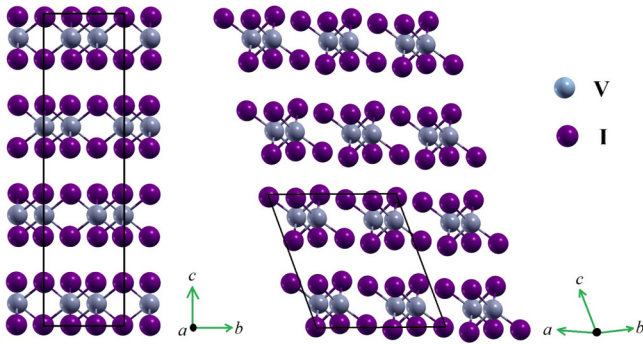


FIG. 1. Schematic representation of the rhombohedral (left panel) and monoclinic (right panel) crystal structural phases of VI_3 bulk crystal. Black lines represent the unit cells.

DFT+DMFT studies [19,20], the dynamical quantum nature of the paramagnetic electronic state of monoclinic VI_3 bulk crystal has not been explored yet. Motivated thereby, in this work we extend our earlier studies on Cr_3 vdW crystals [23] to perform a detailed analysis for the electronic structure reconstruction of rhombohedral and monoclinic VI_3 bulk crystal within the DFT + DMFT approximation [24], showing the emergent correlated electronic state with distinct orbital-selective many-particle fingerprints. As in Refs. [19,20,23], our study highlights the importance of incorporating dynamical MO correlation effects within the five V-3d orbitals to determine the Mott localized electronic state [19,20] induced by MO electronic correlations and the role played by electron doping on the electronic structure reconstruction of VI_3 vdW bulk crystal. Finally, we notice here that attempts to explain the insulating electronic state of VI_3 have been reported in recent years. Reference [18] has proposed that electronic localization arises from orbital-ordered phases accompanying the lattice distortion. This scenario has been ruled out in the work by Sant *et al.* [14], pointing out that the energy splitting associated to distortion underestimates the experimental band gap and suggesting that the insulating ground state is stabilized by Mott correlation effects rather than the Jahn–Teller mechanism. Reference [24], on the other hand, has ascribed the gap opening in VI_3 to combined effects of spin-orbit coupling (SOC) and on-site Hubbard U correlations. However, similar to earlier DFT + DMFT studies on the rhombohedral structural phase of Cr_3 crystals [23], the dynamical Mott-Hubbard mechanism has been confirmed for rhombohedral VI_3 in Refs. [19,20]. Motivated by these DFT + DMFT studies, here we focused on the emergence of Mott localization in the electronic structure reconstruction paramagnetic VI_3 bulk crystal [6], showing the robustness of the $U = 5.0$ eV Mott gap upon electron doping the monoclinic parent compound [13,25].

II. RESULTS AND DISCUSSION

The DFT calculations were performed for the paramagnetic electronic state of rhombohedral and monoclinic structural phases of VI_3 parent compound (see Fig. 1) using the siesta *ab initio* simulation package [26]. Generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof

(PBE) implementation [27] was applied as the exchange correlation functional. Norm-conserving pseudopotentials of Troullier-Martins [28] in Kleinman-Bylander nonlocal form were used to represent the ionic core potential. The Kohn-Sham orbitals [29] are expanded in a linear combination of atomic orbitals of finite range, which is determined by a common confinement energy shift of 0.01 Ry [30]. The precision of the real-space grid integration is determined by an energy cutoff of 200 Ry [31]. The respective Brillouin zone is sampled by a $10 \times 10 \times 10$ Monkhorst-Pack grid [32] for a primitive cell of bulk VI_3 . Finally, as in Ref. [23], the atomic positions were fully optimized until all the force components became smaller than 0.03 eV/Å.

While DFT and DFT + U calculations have provided reliable information regarding structural and magnetic ground-state properties for VI_3 [15,17,21] and analogs [33], they are known to generically fail to capture dynamical electron-electron correlation effects [19,20], and so they cannot access the formation of coherent Kondo quasiparticles and incoherent Hubbard satellites (local moments) at low and high energies [34], respectively. Combining DFT with DMFT is a many-particle prescription for overcoming this problem [35]. Thus, as common to correlated materials within GGA, the one-electron part of the MO Hamiltonian for VI_3 reads $H_0 = \sum_{\mathbf{k},a,\sigma} \epsilon_a(\mathbf{k}) c_{\mathbf{k},a,\sigma}^\dagger c_{\mathbf{k},a,\sigma}$, where $a = (xy, xz, yz, x^2 - y^2, 3z^2 - r^2)$ denotes its diagonalized 3d orbitals and $\epsilon_a(\mathbf{k})$ is the corresponding band dispersion, which encodes details of the one-electron band structure. These five V-3d orbitals are the relevant one-particle inputs for MO-DMFT, which generates a strongly correlated paramagnetic electronic state as shown below. Similar to Ref. [23], the full many-body Hamiltonian for VI_3 bulk crystal reads $H_{\text{int}} = U \sum_{i,a} n_{i,a,\uparrow} n_{i,a,\downarrow} + U' \sum_{i,a \neq b} n_{i,a} n_{i,b} - J_H \sum_{i,a \neq b} \mathbf{S}_{i,a} \cdot \mathbf{S}_{i,b}$. Here $U' = U - 2J_H$ is the interorbital Coulomb interaction term and J_H is the Hund's coupling. We evaluate the many-particle Green's functions $[G_{\mathbf{k},a,\sigma}(\omega)]$ of the correlated many-particle Hamiltonian of VI_3 bulk crystal within DFT + DMFT [35], using MO iterated perturbation theory (MO-IPT) as impurity solver [36]. The DMFT solution involves replacing the lattice model by a self-consistently embedded MO-Anderson impurity model and the self-consistency condition requiring the local impurity Green's function to be equal to the local Green's function for the lattice. The full set of equations for the MO case can be found in Ref. [36], so we do not repeat the equations here. Our real frequency MO-IPT scheme has a proven record of good semiquantitative agreements with experiment for a range of correlated materials, and it gives results for the orbital-selective spectral functions of VI_3 in qualitative accord with quantum Monte Carlo (QMC) calculations [20], as shown below.

A. Role of MO correlations in rhombohedral VI_3

To begin with, in Fig. 2 we show the orbital-resolved DFT density of states (DOS) of the rhombohedral ($R\bar{3}$) structural phase of paramagnetic VI_3 bulk crystal. Owing to the octahedral environment of the V sites, the 3d states split into low-lying t_{2g} and high-lying e_g groups. These two groups are composed by twofold degenerated $t_{2g^2}(\equiv xz, yz)$ and

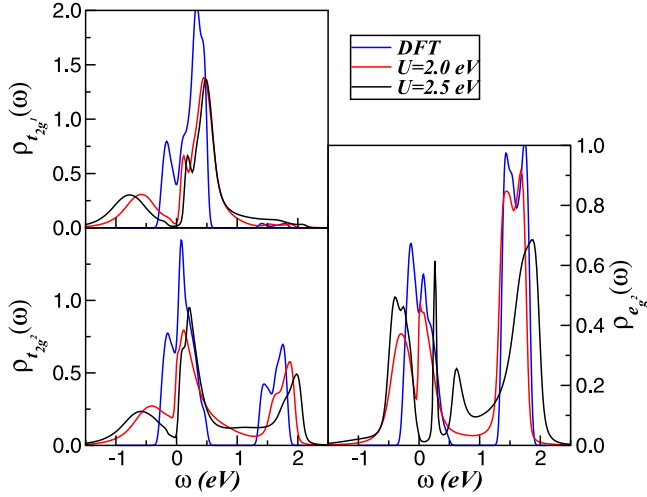


FIG. 2. DFT and DFT + DMFT orbital-resolved density of states (DOS) of rhombohedral VI_3 parent compound, which are composed by two t_{2g}^2 and e_g^2 doublet and a t_{2g}^1 singlet orbitals. Important features to be seen are the narrow bare bandwidths and the fact that all bands in DFT span near the Fermi level, $E_F = \omega = 0$. Also noteworthy is the evolution of orbital-resolved DOS with increasing the on-site Coulomb interaction U .

$e_g^2(\equiv x^2 - y^2, 3z^2 - r^2)$ orbitals and a nondegenerated $t_{2g}^1(\equiv xy)$ orbital, similar to Cr_3 vdW compounds [23]. As seen in Fig. 2, all V-3d orbitals are partially occupied for the V^{3+} electronic configuration with two total valence electrons ($n = 2.0$), in turn resulting in an $S = 1$ spin state within the ferromagnetically ordered phase [22]. Consistent with DFT studies for the nonmagnetically ordered phase of rhombohedral VI_3 bulk crystal [19,20], our GGA results in Fig. 2 show that the active electronic states in this rhombohedral vdW system involve the V 3d carriers, where all d bands have appreciable weight near the Fermi level ($E_F = \omega = 0.0$ eV), implying metallicity at the one-particle DFT level. However, as shown in Fig. 2, MO electron-electron interactions scatter electrons at each orbital and among different orbital channels *via* intra- and interorbital Coulomb interactions and the Hund's exchange parameter J_H [19,20], strongly renormalizing the GGA one-particle spectral functions. As shown in Fig. 2, at $U = 2.5$ eV and $J_H = 0.7$ eV, rhombohedral VI_3 can be characterized as an orbital-selective metal with coexisting insulating (t_{2g}^1, e_g^2) and pseudogap (t_{2g}^2) states.

Let us now turn our attention to our DFT + DMFT(MO-IPT) results obtained upon increasing the on-site U within the formal V^{3+} oxidation state of the VI_3 rhombohedral parent compound. As shown in Fig. 3, the orbital-selective electronic state shown in Fig. 2 smoothly evolves into a paramagnetic Mott insulating state, which sets in close to $U = 4.0$ eV. As seen in this figure, at this U value, all orbital sectors display a Mott-Hubbard gap at E_F . In spite of orbital-selective transfer of spectral weight, lower (LHB) and upper (UHB) Hubbard bands at high energies are visible in a more or less pronounced way, depending on the orbital character, in all orbital-resolved spectral functions. This behavior highlights the intrinsic tendency toward large transfer of spectral

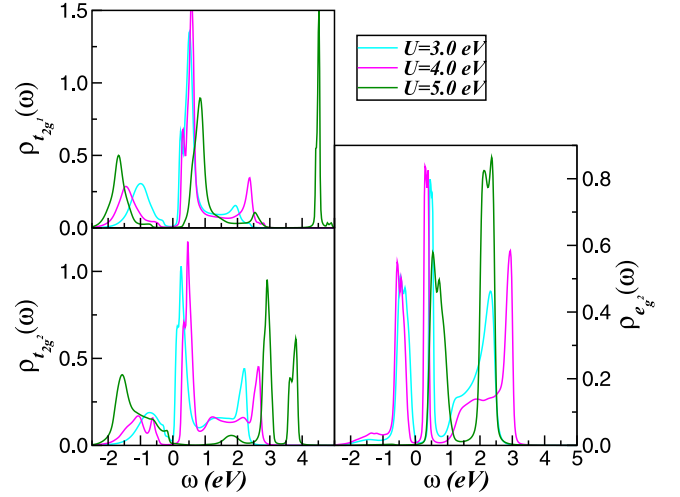


FIG. 3. Evolution of the orbital-resolved DFT + DMFT DOS for the V 3d orbitals of rhombohedral VI_3 . Noteworthy is the strong electronic reconstruction and the formation of narrow upper Hubbard bands and the emergent Mott-localized state on all orbitals at low and high energies, respectively, due to strong dynamical transfer of spectral weight within DMFT.

weight in transition-metal compounds, where the U/W ratio is sizable. Also interesting is the full orbital polarization obtained for the high-energy e_g^2 orbitals at $U = 5.0$ eV, similar to that reported in Ref. [20]. To understand the seeds behind this electronic structure reconstruction, in Fig. 4 we show the corresponding orbital-resolved self-energy imaginary parts associated with the active 3d orbitals of rhombohedral VI_3 vdW crystal. Comparing our results to that reported, for example, for the body-centered tetragonal phase of NbO_2 [37] or to that reported for LaCoO_3 [38], we notice similar features in these different transition-metal systems, i.e., the absence of

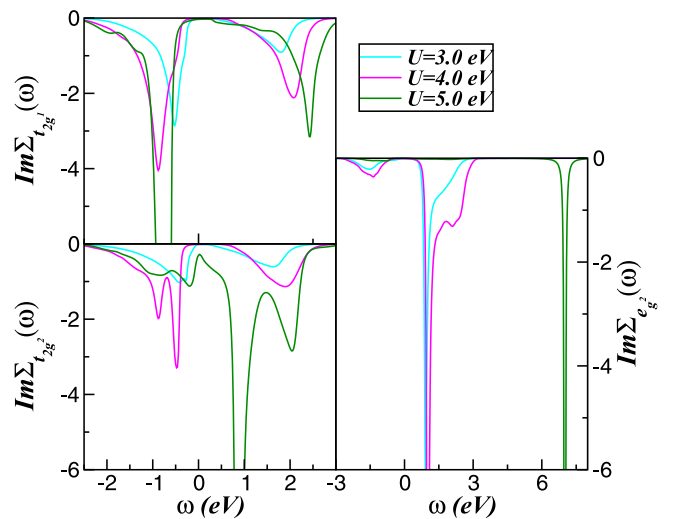


FIG. 4. Orbital-resolved self-energy imaginary parts of rhombohedral VI_3 bulk crystal, showing their evolution with increasing U . A particular feature to be seen is the clearly visible particle-hole asymmetry and the strong frequency dependence at the self-energy pole structures.

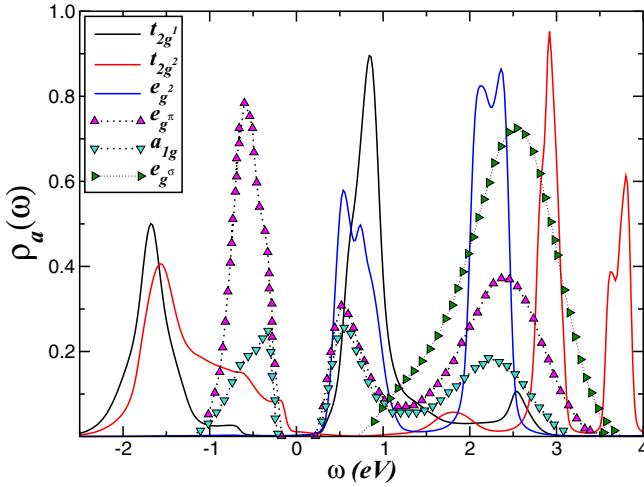


FIG. 5. Comparison between our orbital-resolved DFT + DMFT(MO-IPT) DOS obtained for $U = 5.0$ eV (solid lines) and extant DFT + DMFT [20] results (dotted lines) obtained for the paramagnetic state of rhombohedral VI_3 vdW bulk crystal, showing good qualitative agreement in spite of the different DFT schemes, impurity solvers, and model parameters used in the DMFT calculations. A particular feature to be seen is the full orbital polarization of the high-in-energy e_g^2 channel.

poles at E_F and the strong particle-hole asymmetry in $\Sigma_a(\omega)$. This particle-hole asymmetry is manifested by the appearance of peaks below and/or above E_F in $\text{Im}\Sigma_a(\omega)$. Taken together, our results and those obtained using DFT plus cluster-DMFT calculations [37], for example, a remarkable aspect stands out: $\text{Im}\Sigma_a(\omega)$ in Fig. 4 vanishes for $U = 4.0$ eV in the region of the Mott gap, instead of having a pole as would occur in a conventional Mott insulator. Interesting as well are our results obtained for $U = 5.0$ eV, where as a result of full orbital polarization, only a sharp pole at 7.0 eV above E_F is resolved for $\Sigma_{e_g^2}(\omega)$. This pole structure obtained in a strongly polarized orbital results from U' -induced MO hole-hole scattering processes in the correlated many-particle problem.

To see whether our strongly correlated electronic reconstruction is consistent with extant DFT + DMFT calculations, in Fig. 5 we present a direct comparison between our zero-temperature (T) MO-IPT results obtained for $U = 5.0$ eV and the finite- T DFT + DMFT results reported in Ref. [20]. As seen, good qualitative agreement is obtained in spite of the different DFT + DMFT implementations. To be more specific, apart from the full e_g^2 orbital polarization, the Mott gap in these DFT + DMFT calculations is very close and consistent with the experimental value of 0.6 eV reported in Ref. [6]. These combined results provide a fundamental microscopic support to the fact that experimentally, VI_3 is insulating even at room temperature in the paramagnetic state [5,6], meaning that magnetic order cannot be responsible for the gap at room temperature. This in turn confirms that VI_3 is a Mott insulator with similarities akin to CrI_3 [39] and analogs [23].

B. Role of MO correlations in monoclinic VI_3

Let us now consider the electronic structure of monoclinic VI_3 bulk crystal. Similar to Fig. 2 of the previous section,

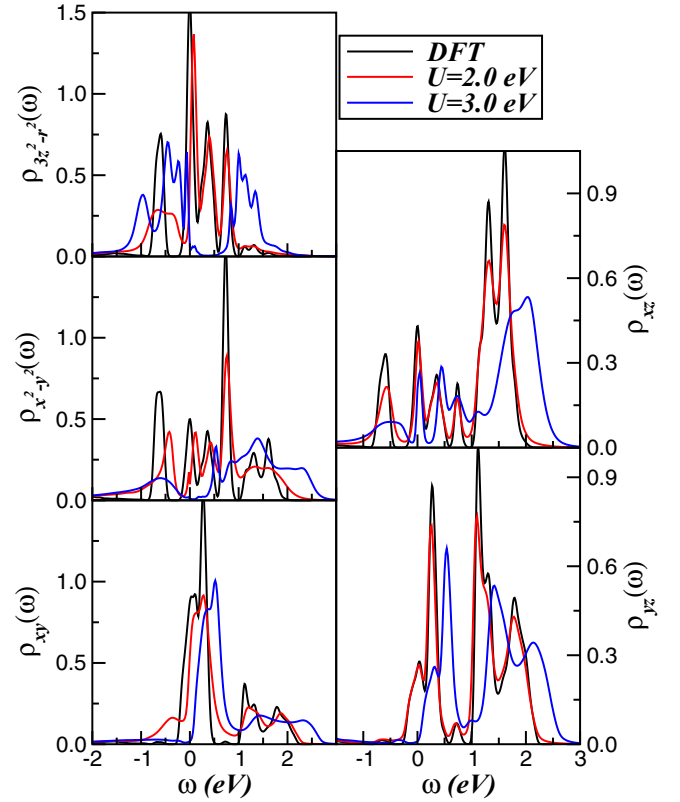


FIG. 6. DFT and DFT + DMFT orbital-resolved DOS of monoclinic VI_3 parent compound. Important features to be seen is the orbital selectivity with narrow band states and the fact that all orbitals in DFT span near the Fermi level. This latter confirms that the electronic states relevant to vanadium trihalides are the V-3d states. Also noteworthy is the electronic reconstruction with clearly visible dynamical transfer of spectral weight with increasing U .

in Fig. 6 we present the orbital-resolved DFT DOS within the $C2/m$ structural phase of paramagnetic VI_3 bulk crystal. Interestingly, different to the rhombohedral phase, the 3d states split into low-lying e_g and high-lying t_{2g} groups in the monoclinic lattice structure. Thus, differently to what is commonly found in transition-metal compounds, the e_g states of the $C2/m$ phase of VI_3 are lower in energy (see our discussion below) and therefore not strongly polarized within GGA. However, as shown Figs. 6 and 7, strong MO electron-electron interactions will strongly renormalize the orbital-resolved spectral functions *via* intrinsic intra- and interorbital Coulomb interactions and the Hund's exchange parameter J_H [19,20]. Particularly relevant in this context is the correlation-induced orbital polarization within the xy, yz orbitals, which are dynamically transferred to energies above E_F , as shown in Fig. 6. Also interesting in this figure is the orbital-selective localization with coexisting Mott-localized e_g orbitals and itinerant xz states.

To gain additional insights on the electronic structure reconstruction of monoclinic VI_3 , in Fig. 7 we display the effect of MO dynamical correlations on the orbital-resolved spectral functions upon further increasing the on-site U , for fixed $J_H = 0.7$ eV, as in Fig. 6. Importantly, our result for $U = 5.5$ eV confirms that monoclinic VI_3 is a paramagnetic

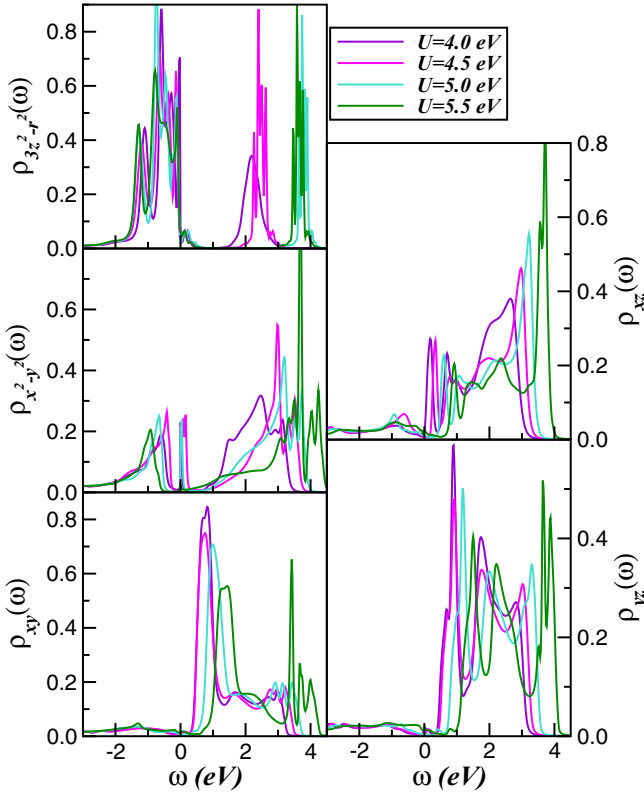


FIG. 7. Effect of multiorbital dynamical correlations in the orbital-resolved DFT + DMFT DOS of monoclinic VI_3 bulk crystal upon increasing the on-site U . Noteworthy is the electronic reconstruction and the emergence of full Mott localization at low energies, due to strong dynamical transfer of spectral weight within DMFT.

Mott insulator, where all orbitals display a Mott-Hubbard gap at E_F . Moreover, as seen in Fig. 7, up to $U = 5.0$ eV monoclinic VI_3 crystal is predicted to host $x^2 - y^2$, xz -Kondo-like quasiparticles [34] at low energies. While the e_g orbitals display clear incoherent Hubbard bands relevant for the local moment formation in VI_3 , the LHB within the t_{2g} orbital sector are nearly depleted due to dynamical electron transfer from the valence to the conduction bands. Additionally, in Fig. 8 we show the energy dependence of the self-energy imaginary parts associated with the active $3d$ orbitals of monoclinic VI_3 vdW crystal. As seen and similar to our results for rhombohedral VI_3 , our results reveal the absence of poles at E_F accompanied by clearly visible particle-hole asymmetry in $\Sigma_a(\omega)$. This might be a hidden intrinsic feature of paramagnetic VI_3 vdW crystal that could be probed in future angle-resolved photoemission (ARPES) studies.

For the sake of completeness, in Fig. 9 we display the U dependence of the on-site orbital occupations $n_{a,\sigma}$ (main panel) and orbital energies (inset), computed using the orbital-resolved spectral functions of monoclinic VI_3 . Similar to Ref. [40], we observe clear changes in orbital polarization with increasing U . These responses are characteristic of strongly correlated electron systems, where the changes in the orbital occupation are linked to dynamical fluctuations in the reconstructed electronic state. Notably, orbital polarization increases with increasing U , driving changes in the correlated

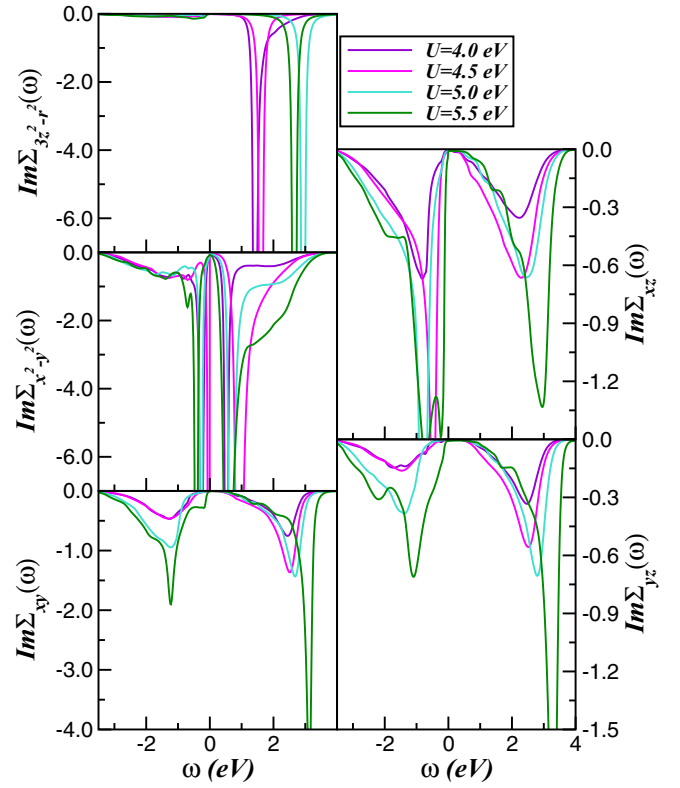


FIG. 8. Orbital-resolved self-energy imaginary parts of monoclinic VI_3 bulk crystal, showing their evolution with increasing U . A particular feature to be seen is the clearly visible particle-hole asymmetry.

spectral functions as shown in Figs. 6 and 7. Our results in Fig. 9 imply a continuous enhancement of ferro-orbital order due to a U' -induced strong interorbital proximity effect,

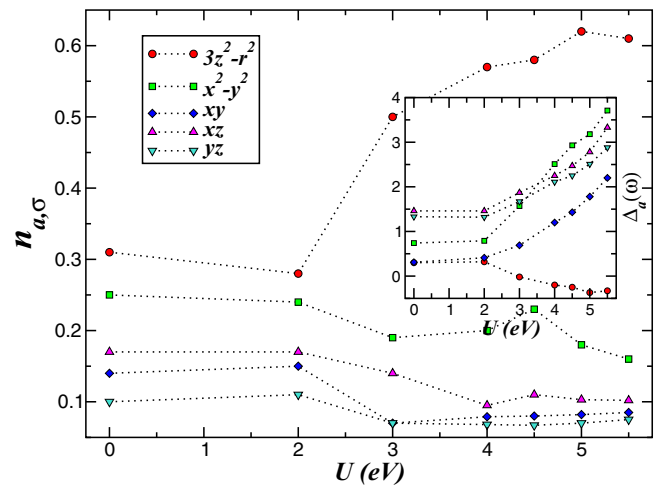


FIG. 9. Orbital occupations $n_{a,\sigma}$ as a function of the on-site U . Notice the changes of the orbital polarization upon increasing U and its increase within the $3z^2 - y^2$ orbital sector starting at $U = 2.0$ eV. Inset shows the evolution of the on-site orbital energies Δ_a as a function of U . An important feature to be seen is the reduction of $\Delta_{3z^2-r^2}$ at finite U .

with the spectral weight being continuously removed from the xy , yz , $x^2 - y^2$ and transferred to the $3z^2 - r^2$ orbital sector in spite of the $S = 1$ spin state, an effect which could be the primary origin of enhanced orbital magnetization [19] with large orbital magnetic moment [15] reported for VI_3 . Also interesting are our results in the inset of Fig. 9 showing the evolution of the on-site orbital energies Δ_a , or the center of gravity of the correlated spectral functions, as a function of U . As seen, with increasing U DFT + DMFT severely renormalizes the center of gravity of each orbital, promoting changes in the correlated spectral functions as displayed in Figs. 6 and 7. This fact, generic to MO systems, is an interesting manifestation of correlation-induced orbital rearrangement and controls the changes of the correlated electronic spectra across the Mott transition. Due to particle-hole asymmetry and anisotropic DFT one-particle energies and hoppings, MO correlations reconstruct the $3d$ orbitals of monoclinic VI_3 vdW crystal in different ways, leading to intrinsic orbital selectivity. Within DFT + DMFT, this orbital-selective mechanism involves two steps: first, static (MO Hartree) renormalization shifts the $3d$ bands relative to each other by amounts depending upon their bare on-site orbital energies and occupations. Second, dynamical MO effects of U , U' , and J_H induce large dynamical spectral weight transfer over wide energy scales. This result implies that in correlated electron systems small variations of U drive appreciable spectral weight transfer, producing orbital-selective changes of the one-site energies. As seen in Fig. 9, the $3z^2 - r^2$ orbital is the most severely affected, implying that this is the strongest correlated channel of monoclinic VI_3 due to its proximity to a half-filling electronic configuration. Future experimental studies are called for to corroborate this prediction.

To make contact with experiments reporting chemical insertion of Li in VI_3 [13,25], in Fig. 10 we show the effect of electron doping ($n = 2.0 + \delta$) on the DFT + DMFT electronic structure obtained for $U = 5.0$ eV (main panels) and $U = 4.5$ eV (insets) for monoclinic VI_3 in Fig. 8. While for the rhombohedral structural phase (not shown) the electronic structure reconstruction upon electron doping is of orbital-selective Mott type, for the monoclinic phase our results for $U = 5.0$ eV reveal a persistent MO Mott state [41] with strongly anisotropic and orbital-dependent Mott-gap-like features at low energies. Particularly interesting here is the robustness of the valence-band dispersion $3z^2 - r^2$ orbital, showing almost no changes to electron doping for the two U values considered in Fig. 10 due to its strongly correlated electronic nature, which is predicted to forbid electron transfer upon lithiation [13,25]. As seen in the main panels of Fig. 10, electron doping mostly enhances the $x^2 - y^2$, xy orbital filling, suggesting that the electron correlations are weak in these channels of monoclinic VI_3 . Taken together, our results in Fig. 10 show that strongly and weakly hot and cold spots in the Fermi surface [42] can be tuned in monoclinic VI_3 crystal via electron doping the parent compound. They also seem to suggest that the shape of the Mott gap and Hubbard bands in this electron-doped structural phase would be anisotropic and orbital dependent. Importantly, these results can be taken as an evidence that MO Coulomb perturbations might pave the way to approach a persistent Mott state in strongly correlated electron systems [41]. If our proposal is to hold, the insulating

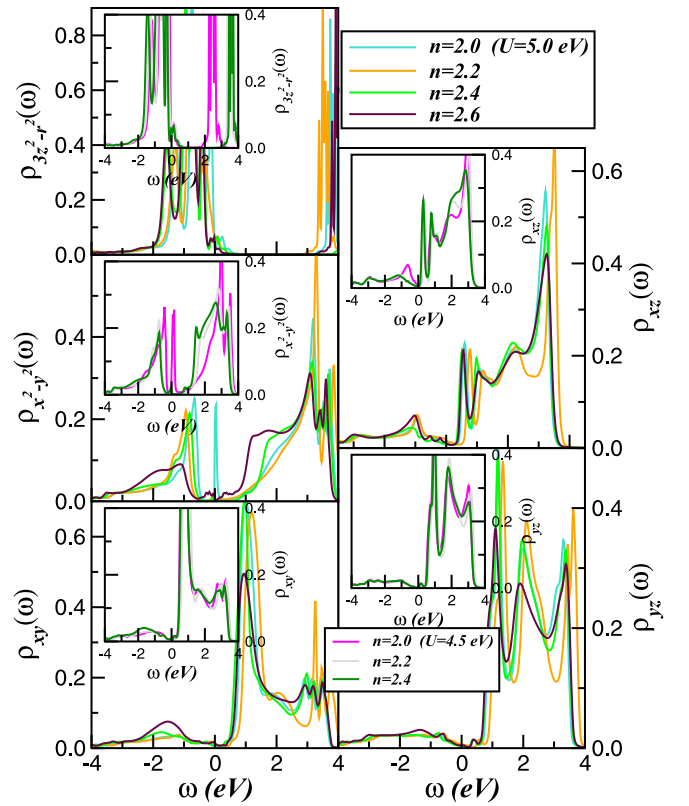


FIG. 10. Orbital-resolved DFT + DMFT (with $U = 5.0$ eV and $J_H = 0.7$ eV) DOS for the V-3d orbitals of electron-doped ($n = 2.0 + \delta$) VI_3 . Notice the robustness of the Mott localized state to electron doping the parent compound. Insets show the changes in the $U = 4.5$ eV DFT + DMFT DOS as a function of the total band filling n .

state in monoclinic Li_xVI_3 ($0 \leq x \leq 0.6$) is predicted to be composed of Fermi surfaces with distinct orbital textures [43], and future spectroscopic experiments could verify this aspect.

III. CONCLUSION

In summary, in this work we have performed a GGA and GGA + DMFT study of electronic structure in a V-contained van der Waals bulk crystal. Using realistic local interaction parameters for the five-orbital Hubbard model, we provide a microscopic description of the excitation spectrum which emerges within the nonmagnetically ordered state of VI_3 . Together with theory [19,20] and experimental [5,6] studies, we reveal the true nature of the Mott insulating state of VI_3 . An important message of our approach is to show that a strong coupling picture leads to a persistent Mott state [41] upon electron doping the monoclinic parent compound, which might be relevant for future studies on Li-doped VI_3 [13,25]. Our theoretical analysis provides support for the dynamical electronic structure reconstruction in transition-metal trihalides in their different structural phases, and it is expected to be generally applicable to understanding orbital selectivity in strongly interacting electron systems and the underlying electronic state which may emerge in the paramagnetic state of van der Waals magnetic materials [1,44].

ACKNOWLEDGMENTS

L.C.'s work is supported by CNPq (Grant No. 303359/2024-2). Acknowledgment is also made (L.C.) to FINEP (Project No. 0167/25) as well as (L.C. and S.S.C.) to CAPES.

DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

-
- [1] K. F. Mak, J. Shan, and D. C. Ralph, Probing and controlling magnetic states in 2D layered magnetic materials, *Nat. Rev. Phys.* **1**, 646 (2019); M. Gibertini, M. Koperski, A. F. Morpurgo, and K. S. Novoselov, Magnetic 2D materials and heterostructures, *Nat. Nanotechnol.* **14**, 408 (2019).
- [2] B. Huang, G. Clark, E. Navarro-Moratalla, D. R. Klein, R. Cheng, K. L. Seyler, D. Zhong, E. Schmidgall, M. A. McGuire, and D. H. Cobden, Layer-dependent ferromagnetism in a van der Waals crystal down to the monolayer limit, *Nature (London)* **546**, 270 (2017); C. Gong, L. Li, Z. Li, H. Ji, A. Stern, Y. Xia, T. Cao, W. Bao, C. Wang, and Y. Wang, Discovery of intrinsic ferromagnetism in two-dimensional van der Waals crystals, *Science* **363**, eaav4450 (2019); Z. Fei, B. Huang, P. Malinowski, W. Wang, T. Song, J. Sanchez, W. Yao, D. Xiao, X. Zhu, and A. F. May, Two-dimensional itinerant ferromagnetism in atomically thin Fe_3GeTe_2 , *Nat. Mater.* **17**, 778 (2018); K. S. Burch, D. Mandrus, and J.-G. Park, Magnetism in two-dimensional van der Waals materials, *Nature (London)* **563**, 47 (2018); C. Gong and X. Zhang, Two-dimensional magnetic crystals and emergent heterostructure devices, *Science* **363**, eaav4450 (2019); B. Huang, M. A. McGuire, A. F. May, D. Xiao, P. Jarillo-Herrero, and X. Xu, Emergent phenomena and proximity effects in two-dimensional magnets and heterostructures, *Nat. Mater.* **19**, 1276 (2020).
- [3] N. Mounet, M. Gibertini, P. Schwaller, D. Campi, A. Merkys, A. Marrazzo, T. Sohier, I. E. Castelli, A. Cepellotti, and G. Pizzi, Two-dimensional materials from high-throughput computational exfoliation of experimentally known compounds, *Nat. Nanotechnol.* **13**, 246 (2018); S. Haastrup, M. Strange, M. Pandey, T. Deilmann, P. S. Schmidt, N. F. Hinsche, M. N. Gjerding, D. Torelli, P. M. Larsen, and A. C. Riis-Jensen, The computational 2D materials database: High-throughput modeling and discovery of atomically thin crystals, *2D Mater.* **5**, 042002 (2018); D. Torelli, H. Moustafa, K. W. Jacobsen, and T. Olsen, High-throughput computational screening for two-dimensional magnetic materials based on experimental databases of three-dimensional compounds, *npj Comput. Mater.* **6**, 158 (2020); A. Kabiraj, M. Kumar, and S. Mahapatra, High-throughput discovery of high Curie point two-dimensional ferromagnetic materials, *ibid.* **6**, 35 (2020).
- [4] D. Juza, D. Giegling, and H. Schäfer, Über die Vanadinjodide VJ_2 und VJ_3 , *ZAAC* **366**, 121 (1969).
- [5] S. Song, M. J. Coak, N. Lee, J. Kim, T. Y. Kim, H. Hamidov, H. Cho, C. Liu, D. M. Jarvis, P. A. C. Brown, *et al.*, Bulk properties of the van der Waals hard ferromagnet VI_3 , *Phys. Rev. B* **99**, 041402(R) (2019).
- [6] T. Kong, K. Stolze, E. I. Timmons, J. Tao, D. Ni, S. Guo, Z. Yang, R. Prozorov, and R. J. Cava, VI_3 - A new layered ferromagnetic semiconductor, *Adv. Mater.* **31**, 1808074 (2019).
- [7] S. Tian, J.-F. Zhang, C. Li, T. Ying, S. Li, X. Zhang, K. Liu, and H. Lei, Ferromagnetic van der Waals crystal VI_3 , *J. Am. Chem. Soc.* **141**, 5326 (2019).
- [8] J. Dillon, Jr. and C. Olson, Magnetization, resonance, and optical properties of the ferromagnet CrI_3 , *J. Appl. Phys.* **36**, 1259 (1965).
- [9] M. A. McGuire, Cleavable magnetic materials from van der Waals layered transition metal halides and chalcogenides, *J. Appl. Phys.* **128**, 110901 (2020).
- [10] Z. Lin, B. Huang, K. Hwangbo, Q. Jiang, Q. Zhang, Z. Liu, Z. Fei, H. Lv, A. Millis, M. McGuire, D. Xiao, J.-H. Chu, and X. Xu, Magnetism and its structural coupling effects in 2D Ising ferromagnetic insulator VI_3 , *Nano Lett.* **21**, 9180 (2021).
- [11] P. Doležal, M. Kratochvílová, V. Holý, P. Čermák, V. Sechovský, M. Dušek, M. Míšek, T. Chakraborty, Y. Noda, *et al.*, Crystal structures and phase transitions of the van der Waals ferromagnet VI_3 , *Phys. Rev. Mater.* **3**, 121401(R) (2019).
- [12] G.-D. Zhao, X. Liu, T. Hu, F. Jia, Y. Cui, W. Wu, M.-H. Whangbo, and W. Ren, Difference in magnetic anisotropy of the ferromagnetic monolayers VI_3 and CrI_3 , *Phys. Rev. B* **103**, 014438 (2021).
- [13] T. Marchandier, N. Dubouis, F. Fauth, M. Avdeev, A. Grimaud, J.-M. Tarascon, and G. Rousse, Crystallographic and magnetic structures of the VI_3 and LiVI_3 van der Waals compounds, *Phys. Rev. B* **104**, 014105 (2021).
- [14] R. Sant, A. De Vita, V. Polewczyk, G. M. Pierantozzi, F. Mazzola, G. Vinai, G. van der Laan, G. Panaccione, and N. B. Brookes, Anisotropic hybridization probed by polarization dependent x-ray absorption spectroscopy in VI_3 van der Waals Mott ferromagnet, *J. Phys.: Condens. Matter* **35**, 405601 (2023).
- [15] D. Hovancík, J. Pospíšil, K. Carva, V. Sechovsky, and C. Piamonteze, Large orbital magnetic moment in VI_3 , *Nano Lett.* **23**, 1175 (2023).
- [16] L. M. Sandratskii and K. Carva, Interplay of spin magnetism, orbital magnetism, and atomic structure in layered van der Waals ferromagnet VI_3 , *Phys. Rev. B* **103**, 214451 (2021).
- [17] L. Liu, K. Yang, G. Wang, and H. Wu, Two-dimensional ferromagnetic semiconductor VBr_3 with tunable anisotropy, *J. Mater. Chem. C* **8**, 14782 (2020).
- [18] C. Huang, F. Wu, S. Yu, P. Jena, and E. Kan, Discovery of twin orbital-order phases in ferromagnetic semiconducting VI_3 monolayer, *Phys. Chem. Chem. Phys.* **22**, 512 (2020).
- [19] Z. Zhou, S. K. Pandey, and J. Feng, Dynamical correlation enhanced orbital magnetization in VI_3 , *Phys. Rev. B* **103**, 035137 (2021).
- [20] I. V. Solov'yev, R. Ono, and S. A. Nikolaev, Ferromagnetic ferroelectricity due to the Kugel-Khomskii mechanism of orbital ordering assisted by atomic Hund's second rule effects, *Phys. Rev. B* **110**, 205116 (2024).

- [21] T. P. T. Nguyen, K. Yamauchi, T. Oguchi, D. Amoroso, and S. Picozzi, Electric-field tuning of the magnetic properties of bilayer VI_3 : A first-principles study, *Phys. Rev. B* **104**, 014414 (2021).
- [22] X. Zhao and Y. An, Multiple topological phases with electronic correlation in intrinsic ferromagnetic semimetal VI_3 monolayer, *Small* **20**, 2407232 (2024).
- [23] L. Craco, S. S. Carara, Y.-C. Shao, Y.-D. Chuang, and B. Freelon, Mott localization in the van der Waals crystal CrI_3 : A GGA DMFT study, *Phys. Rev. B* **102**, 195130 (2020); Electronic structure of rhombohedral CrX_3 ($\text{X}=\text{Br}, \text{Cl}, \text{I}$) van der Waals crystals, *103*, 235119 (2021).
- [24] G. Kotliar, S. Y. Savrasov, K. Haule, V. S. Oudovenko, O. Parcollet, and C. A. Marianetti, Electronic structure calculations with dynamical mean-field theory, *Rev. Mod. Phys.* **78**, 865 (2006).
- [25] N. Dubouis, T. Marchandier, G. Rousse, F. Marchini, F. Fauth, M. Aydeev, A. Iadecola, B. Porcheron, M. Deschamps, J.-M. Tarascon, and A. Grimaud, Extending insertion electrochemistry to soluble layered halides with superconcentrated electrolytes, *Nat. Mater.* **20**, 1545 (2021); J. Liang, X. Li, J. T. Kim, X. Hao, H. Duan, R. Li, and X. Sun, Halide layer cathodes for compatible and fast-charged halides-based all-solid-state Li metal batteries, *Angew. Chem. Int. Ed.* **62**, e20221708 (2023).
- [26] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, The SIESTA method for ab initio, order- N materials simulation, *J. Phys.: Condens. Matter* **14**, 2745 (2002); E. Artacho, E. Anglada, O. Dieguez, J. D. Gale, A. García, J. Junquera, M. Martin, P. Ordejón, J. M. Pruneda, D. Sánchez-Portal, and J. M. Soler, The SIESTA method, developments and applicability, *ibid.* **20**, 064208 (2008).
- [27] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [28] N. Troullier and J. L. Martins, Efficient pseudopotentials for plane-wave calculations, *Phys. Rev. B* **43**, 1993 (1991).
- [29] W. Kohn and L. J. Sham, Self-consistent equations including exchange and correlation effects, *Phys. Rev.* **140**, A1133 (1965).
- [30] J. Junquera, Ó. Paz, D. Sánchez-Portal, and E. Artacho, Numerical atomic orbitals for linear-scaling calculations, *Phys. Rev. B* **64**, 235111 (2001).
- [31] J. Moreno and J. M. Soler, Optimal meshes for integrals in real- and reciprocal-space unit cells, *Phys. Rev. B* **45**, 13891 (1992).
- [32] H. J. Monkhorst and J. D. Pack, Special points for Brillouin-zone integrations, *Phys. Rev. B* **13**, 5188 (1976).
- [33] D. Mastrippolito, L. Camerano, H. Swiatek, B. Smíd, T. Klimczuk, L. Ottaviano, and G. Profeta, Polaronic and Mott insulating phase of layered magnetic vanadium trihalide VCl_3 , *Phys. Rev. B* **108**, 045126 (2023).
- [34] A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Dynamical mean-field theory of strongly correlated fermion systems and the limit of infinite dimensions, *Rev. Mod. Phys.* **68**, 13 (1996).
- [35] K. Yang, F. Fan, H. Wang, D. I. Khomskii, and H. Wu, VI_3 : A two-dimensional Ising ferromagnet, *Phys. Rev. B* **101**, 100402(R) (2020).
- [36] L. Craco, Quantum orbital entanglement: A view from the extended periodic Anderson model, *Phys. Rev. B* **77**, 125122 (2008).
- [37] W. H. Brito, M. C. O. Aguiar, K. Haule, and G. Kotliar, Dynamic electronic correlation effects in NbO_2 as compared to VO_2 , *Phys. Rev. B* **96**, 195102 (2017).
- [38] H. Park, R. Nanguneri, and A. T. Ngo, DFT DMFT study of spin-charge-lattice coupling in covalent LaCoO_3 , *Phys. Rev. B* **101**, 195125 (2020).
- [39] M. A. McGuire, H. Dixit, V. R. Cooper, and B. C. Sales, Coupling of crystal structure and magnetism in the layered, ferromagnetic insulator CrI_3 , *Chem. Mater.* **27**, 612 (2015).
- [40] A. Liebsch, H. Ishida, and G. Bihlmayer, Coulomb correlations and orbital polarization in the metal-insulator transition of VO_2 , *Phys. Rev. B* **71**, 085109 (2005); H. Park, A. J. Millis, and C. A. Marianetti, Influence of quantum confinement and strain on orbital polarization of four-layer LaNiO_3 superlattices: A DFT DMFT study, *ibid.* **93**, 235109 (2016); L. Craco and S. Leoni, Orbital-selective mixed-valent Mott/metal phase coexistence in NdNiO_2 films, *Phys. Rev. Mater.* **7**, 044802 (2023); M. R. Norman, A. S. Botana, J. Karp, A. Hampel, H. LaBollita, A. J. Millis, G. Fabbri, Y. Shen, and M. P. M. Dean, Orbital polarization, charge transfer, and fluorescence in reduced-valence nickelates, *Phys. Rev. B* **107**, 165124 (2023).
- [41] T. Aoyama, K. Ohta, K. Shimizu, and K. Ohgushi, Persistent spin-orbit Mott insulating state in highly compressed post-perovskite CaIrO_3 , *J. Phys. Soc. Jpn.* **91**, 045003 (2022); G. Zhang, H. Hadipour, and E. Pavarini, Nature of the high-pressure insulating state in Sr_2IrO_4 : Mott picture, *Phys. Rev. B* **111**, L121101 (2025).
- [42] J. Fink, J. Nayak, E. D. L. Rienks, J. Bannies, S. Wurmehl, S. Aswartham, I. Morozov, R. Kappenberger, M. A. ElGhazali, L. Craco, H. Rosner, C. Felser, and B. Buchner, Evidence of hot and cold spots on the Fermi surface of LiFeAs , *Phys. Rev. B* **99**, 245156 (2019).
- [43] S. Beaulieu, M. Schueler, J. Schusser, S. Dong, T. Pincelli, J. Maklar, A. Neef, F. Reinert, M. Wolf, L. Rettig, J. Minár, and R. Ernstorfer, Unveiling the orbital texture of $1T\text{-TiTe}_2$ using intrinsic linear dichroism in multidimensional photoemission spectroscopy, *npj Quantum Mater.* **6**, 93 (2021); S. Han, H.-W. Lee, and K.-W. Kim, Microscopic study of orbital textures, *Curr. Appl. Phys.* **50**, 13 (2023); Q. Gao, H. Chen, W.-S. Lu, Y.-H. Chan, Z. Chen, Y. Huang, Z. Liu, and P. Chen, Orbital textures and evolution of correlated insulating state in monolayer $1T$ phase transition metal dichalcogenides, *Nat. Commun.* **16**, 3784 (2025).
- [44] S. O. Valenzuela and S. Roche, The phase diagram of 2D antiferromagnets, *Nat. Nanotechnol.* **14**, 1088 (2019).