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Valence and Conduction Band Structure of a Quasi-2D Semiconductor SnS₂

David A. Racke,¹ Mahesh R. Neupane,^{2,*} and Oliver L. A. Monti^{1,3,*}

¹*University of Arizona, Department of Chemistry & Biochemistry, 1306 E. University Blvd.,
Tucson, AZ 85721, USA*

²*Macromolecular Science & Technology Branch, U.S. Army Research Laboratory, Aberdeen
Proving Ground, Maryland 21005, USA*

³*University of Arizona, Department of Physics, 1118 E. Fourth Street, Tucson, AZ 85721, USA*

e-mail address: mahesh.neupane.ctr@mail.mil, monti@u.arizona.edu

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Tel: ++1 520 626 1177

Fax: ++1 520 621 8407

Abstract:

We present a momentum-resolved photoemission spectroscopy study of both the valence and conduction band region in the quasi-two dimensional van der Waals-layered indirect bandgap semiconductor SnS₂. Using a combination of angle-resolved ultraviolet photoemission (ARUPS) and angle-resolved two-photon photoemission (AR-2PPE), we characterize the band structure of bulk SnS₂. Comparison with density functional theory calculations shows excellent quantitative agreement in the valence band region and reveals several localized bands that originate likely from surface defects such as sulfur vacancies. Evidence for a moderate density of surface defects is also observed by AR-2PPE in the conduction band region, leading to localized bands not present in the computational results. The energetic structure and dispersion of the conduction bands is captured well by the computational treatment, with some quantitative discrepancies remaining. Our results provide a broader understanding of the electronic structure of SnS₂ in particular and van der Waals layered semiconductors in general.

1 Introduction

Layered van der Waals materials have recently drawn significant attention for their unusual and highly thickness-dependent properties [1–4]. Due to the strongly anisotropic electronic structure, striking new physical properties have been discovered, particularly in the few-layer limit, and for a wide variety of materials ranging from graphene to transition metal dichalcogenides (TMDCs) such as MoS₂ [5–7]. For this reason, renewed attention has been drawn to the multilayer and bulk properties of these materials [8–14].

Electronic structure is experimentally most directly accessed via momentum-resolved photoemission spectroscopy. This has been used for band structure measurements for a number of bulk layered materials [15], and more recently also for select materials in the few-layer limit [9,14,16]. The majority of these reports rely on standard photoemission spectroscopies and focus therefore on the occupied levels and the valence band structure. Particularly lacking is however a detailed experimental consideration of the unoccupied part of the band structure of layered materials. Although the conduction band and higher lying bands can be observed by angle-resolved inverse photoemission spectroscopy (AR-IPES) across a wide range of momentum space [17], the spectral resolution is somewhat poor, limiting a detailed analysis of the electronic structure. Angle-resolved two-photon photoemission (AR-2PPE) constitutes an excellent alternative, offering high spectral resolution and the ability to probe in principle also ultrafast carrier dynamics, in exchange for accessing only part of k -space due to the low kinetic energies of the photoemitted electrons [18].

Except in the case of graphene and TiSe₂ [19–21], AR-2PPE has however not yet been used to investigate the unoccupied part of the band structure in layered materials. Such investigations are necessary to test state-of-the-art computational treatments of van der Waals materials, invaluable to understand carrier physics in the 2D and quasi-2D limit. Here, we

demonstrate for the first time that this approach is feasible for the quasi-2D layered metal dichalcogenide SnS_2 and report a comprehensive study of the valence and conduction band structure by angle-resolved ultraviolet photoemission (ARUPS), AR-2PPE and high-level density functional theory (DFT) calculations.

We focus here on SnS_2 , a van der Waals layered bulk semiconductor with an indirect bandgap of 2.3 eV [22]. SnS_2 has attracted long-standing interest for energy harvesting, storage and photocatalytic water splitting applications both at the bulk and the nanoparticle level [2,23–26], driven in part by the earth abundance of both Sn and S. To take full advantage of the unique electronic properties in the single and few-layer limit, Huang *et al.* investigated carrier transport in field effect transistors, achieving mobilities in excess of $5 \text{ cm}^2/\text{Vs}$ [22]. Recently, hybrid organic semiconductor / SnS_2 structures were investigated as well, highlighting the role of defects in controlling electronic interactions in the interfacial region [27,28]. In order to understand and tailor these properties more comprehensively, it is essential to accurately map the electronic structure of SnS_2 . Several momentum-integrated photoemission studies of SnS_2 exist [22,29,30], complemented by a few momentum-resolved band structure measurements of the valence band [31,32]. The latter have either not been compared to theoretical treatments of SnS_2 or have shown only modest agreement with pseudopotential-based DFT calculations [33]. No momentum-resolved measurements of the conduction band by either AR-2PPE or AR-IPES have been reported thus far.

Here, we present band structure measurements and a computational treatment of the 4H-polymorph of SnS_2 in both the valence and conduction band regions, achieving good agreement between theory and experiment. We find that defect levels, attributed to sulfur vacancies, result in additional levels clearly visible in the band structure. With the AR-2PPE results reported here,

our work constitutes a comprehensive band structure measurement in this layered metal dichalcogenide, and opens avenues towards improved understanding of the carrier physics in quasi-2D and ultimately 2D layered semiconductors.

2 Methods and Materials

SnS₂ crystals of the 4H polymorph were prepared according to methods described previously [22,27,28]. Briefly, SnS₂ was grown by the Bridgman method, and *n*-doped with a carrier concentration of $2.3(1) \times 10^{17} \text{ cm}^{-3}$, as determined by the van der Pauw method [34]. Immediately prior to introduction into an ultrahigh vacuum loadlock, with a base pressure of 1×10^{-9} Torr, the SnS₂ sample was cleaved, followed by pump-down, degassing and annealing at $\sim 250^\circ \text{C}$ for approximately 12 h.

Angle-resolved photoemission spectra were collected at room temperature in a VG Escalab MK II photoelectron spectrometer, base pressure 2×10^{-10} Torr, with an acceptance angle of $\pm 1.5^\circ$. All spectra were referenced to the Fermi energy of the analyzer, which was calibrated using a sputter-cleaned Au foil. All *k*-resolved measurements average over the $\bar{\Gamma}\bar{K}$ and $\bar{\Gamma}\bar{M}$ directions. ARUPS was acquired using a He(I) lamp ($h\nu = 21.2 \text{ eV}$, Specs UVS 10/35, 30° angle of incidence from normal), with a sample bias of -5 V. For AR-2PPE, we used the frequency-tripled output of a 15 W pumped Ti:sapphire oscillator (80 MHz repetition rate, $\sim 100 \text{ fs}$ pulse duration) as the excitation light source. Following dispersion compensation in a prism pair, the pulse train was introduced into the UHV chamber through a fused silica viewport, incident on the sample in p-polarization. Pulse energies were attenuated by a neutral density filter to $\sim 150 \text{ pJ/pulse}$. For these measurements the sample bias was reduced to -3 V. No evidence of surface photovoltage effects or photodamage were observed even after extended exposure. All AR-2PPE

spectra are reported in terms of final state energy E_{final} , which constitutes the total photoelectron energy above the Fermi energy E_F after absorption of two photons.

Density-functional theory (DFT) using the projector augmented wave (PAW) method as implemented in the VASP software package [35] was used to calculate the band structure and density of states (DOS) of SnS₂. In order to circumvent the well-known bandgap underestimation issue of the Perdew-Burke-Ernzerhof (PBE) functional [36–38], the screened Heyd-Scuseria-Ernzerhof (HSE) hybrid functional was employed [39]. A zone-centered Monkhorst-Pack scheme was adopted to integrate over the Brillouin zone with a k -mesh of $8 \times 8 \times 4$ for the SnS₂ structure, and a plane-wave basis kinetic energy cutoff of 300 eV was used. To represent a crystalline solid, periodic boundary conditions (PBC) in all three spatial dimensions are applied. The total energies and Hellmann-Feynman forces on the atoms are converged to 10^{-6} eV and 50 meV Å⁻¹, respectively. The equilibrium cell shape and the volume are determined by optimizing all internal degrees of freedom. Using the optimized lattice parameters, the k -mesh sampling in the Brillouin zone and the plane-wave cutoff energy are tested to ensure that the total energy fluctuations are within 1 meV/atom limit. The primitive cell of SnS₂ structure consists of sheets of Sn atoms in the basal plane, with each Sn atom octahedrally coordinated between close-packed sheets of S atoms. In general, bulk SnS₂ can exist in two different polytypes, denoted in the Ramsdall notation as 2H and 4H. The 2H polytype is the simplest structure with a stacking sequence A γ B-A γ B, where the γ represents Sn atoms. The 4H polytype has a stacking sequence of A γ B-C γ D, with two layers and two molecular units per unit cell [40], as shown in the Fig. 1a.. The in-plane lattice parameters ($a = b$) are nearly equivalent for both polytypes, but the out-of-plane lattice parameter (c) is approximately doubled for the 4H polytype. For SnS₂ crystals used in this study, grown at high temperatures, the 4H polytype is thermodynamically favored, as

confirmed by Raman spectroscopy [22], and we consider only this polytype in the remainder [22,41]. Figure 1a shows the calculated SnS₂ unit cell and lattice dimensions which are in excellent agreement with previous measurements [22]. The lattice constants of SnS₂ were obtained from the Grimme DFT-D3 volume optimized bulk SnS₂ structure [42], and the atomic coordinates were optimized at this fixed lattice constant using the PBE functional. In order to establish confidence in the PBE-generated lattice parameters, they were further optimized using the HSE functional. Both the PBE and HSE functionals yielded lattice constants within $\pm 3\%$ of the experimentally observed values, consistent with earlier studies on other layered materials [43,44]. For the HSE calculations, Hartree-Fock screening and exchange parameters, with the PBE correlation, were set to $0.3 \text{ \AA}^{-1}$ and 25%, respectively, which is known as the HSE03 flavor of the available hybrid functionals within the VASP software package. Space and momentum projected density of states calculations and band structure calculations were performed by integrating over the Brillouin zone with $16 \times 16 \times 8$ k-mesh using the tetrahedron method with Blöchl corrections [45]. The spin-orbit coupling (SOC) is included during density of state and band structure calculation.

3 Results

3.1 SnS₂ valence band structure

To situate the analysis of the ARUPS data, Figure 1b shows an overview of the ARUPS spectra in 5° increments, with the orbital character of the most intense bands indicated. For improved clarity, the background from inelastically scattered secondary electrons was removed by a linear fit to those spectral regions that contain no other strong features. Colored circles indicate the peak center of Gaussian fits to the observed spectral envelopes and thus correspond to spectroscopically identifiable bands or sets of overlapping bands. The top of the SnS₂ valence band region is dominated by a manifold of S 3p-derived levels which span binding energies of -

2.0 to -4.5 eV for the *n*-doped crystal [32]. The S 3p manifold contains at least five distinct, mildly downward dispersing features. Dispersive, lower intensity features are also observed at binding energies ranging from -7 to -11 eV, with the feature at -8 eV (green circle) corresponding to an Sn 5s-derived band [32].

The SnS₂ band structure is obtained in a straightforward manner from these experimental measurements by calculating $k_{||}$, the electronic momentum in the plane of the surface, for each fitted peak:

$$k_{||} = \sqrt{\frac{2m_e E_{\text{kin}}}{\hbar^2}} \sin\vartheta \quad (1)$$

Figure 1: (Color online) a) Structure and atomic arrangement of the 4H polytype of SnS_2 . A, B, and C represent S atoms in the different planes, and γ represents Sn atoms. b) Overview of the angle-resolved UP spectra (~ 21.2 eV) of the SnS_2 valence band region for a selection of photoemission angles and averaged over k_x and k_y . Prior to analysis, background signal from inelastically scattered photoelectrons was removed by a linear least-squares fit to spectral regions without strong features. Colored circles designate peak centers of Gaussian fits to the observed features. Spectra are offset for clarity. c) Valence band structure of SnS_2 , as mapped by ARUPS. d) Calculated DOS and pDOS of SnS_2 . 0 eV corresponds to the VBM in these calculations. Circles represent peak centers of Gaussian fits to experimentally observed features in part b).

where θ is the photoemission angle measured relative to the surface normal, and E_{kin} is the photoelectron kinetic energy. The results of this analysis are plotted in Figure 1c, showing both photoemission intensity and dispersion of each of the identified features.

We next compare our measured band structure and density of states in the valence band region directly with state-of-the-art HSE DFT calculations. This method has been widely used in complex systems and studies of composition-dependent electronic properties of III-V materials [46], structural and magnetic properties in transition-metal perovskites [47] and multilayer TMDCs [48]. Figure 2 shows the direct comparison of experimental and theoretical

results, with generally excellent agreement between the two sets of data. The region of the valence band maximum consists of a large number of closely spaced, mildly dispersive bands that are not resolved experimentally near Γ , but then split up towards the edge of the Brillouin zone. SOC, on the order of ~ 100 meV, leads to “doubling” of the various bands, an effect that is not resolved in the measured band structure. We attribute the minor differences between theory and experiment to a combination of experimental averaging over the $\overline{\Gamma K}$ and $\overline{\Gamma M}$ directions and residual correlation of the spectral fits to the ARUPS data caused by spectral congestion. The agreement between experimental and computational band structures is further confirmed by comparing the ARUP-spectra with the calculated density of states (DOS) in the region of the valence band maximum (Figure 1d). Despite neglecting matrix elements for photoemission in the computational treatment, the calculated DOS and the measured spectra closely resemble each other. The calculated partial DOS (pDOS) shows that the valence band maximum is predominantly made up of S derived bands, while the region of the conduction band minimum is dominated by bands with Sn character, as expected. The valence band at Γ is composed of 94% in-plane S p_x and p_y orbitals, with negligible contributions from out-of-plane orbitals. The conduction band minima, which lies at the M point [22], is composed of 45% Sn 5s orbitals atom and 29% S p_x and p_y orbitals. Thus, the bandgap is expected to remain indirect even in the 2D monolayer limit, as indeed confirmed by recent experiments [22].

Figure 2: (Color online) Comparison of ARUPS peak positions for SnS_2 with the DFT calculated valence band structure. Light gray lines are the calculated band structure from Γ to M, while light blue lines are from Γ to K. Black squares indicate experimentally measured levels that agree well with theory, while the red circles denote experimental peaks that do not appear in the calculated band structure.

The most striking deviation between the measured and the theoretical valence band structure arises in three different largely non-dispersive states that are experimentally observed around -7 eV, -9.8 eV and -10.7 eV. Given the otherwise excellent agreement between measured and calculated band structure for 4H- SnS_2 , these bands arise likely from surface confined states or crystal imperfections not captured in the theoretical treatment. The localization behavior implied by the unique dispersion of these bands suggests that they may in fact originate from small populations of crystal defects, also supported by their low photoemission intensity (Figure 1). Point defects such as sulfur vacancies have been recently observed indirectly in the near-surface region [27,28], and have also been suggested to be responsible for the intrinsic *n*-type character of SnS_2 [49]. We will return to this interpretation in the next section. We may in all cases however exclude adsorbed contaminants as the origin of these bands, since x-ray photoemission spectra showed no species other than Sn and S, nor the presence of either reduced

tin sulfide SnS or metallic tin. Step edges or grain boundaries might be responsible for the more dispersive of the three bands, as was suggested recently for MoS₂ [50–53].

In summary, experimental and theoretical valence band structures for bulk SnS₂ agree well, capturing the essential elements of weak coupling of layered materials. Experimentally, additional strongly localized bands are also observed, likely originating from defects and grain boundaries. The overall excellent agreement in the valence band region provides the necessary framework for a photoemission study of the conduction band region.

3.2 SnS₂ conduction band structure

To probe the electronic structure in the conduction band region, we used AR-2PPE. Figure 3a shows representative AR-2PPE spectra, obtained at Γ and for a range of different photon energies. The spectra are plotted in terms of final state energy E_{final} , which represents the total energy of the electron relative to the Fermi energy E_F after absorption and photoemission. No spectral signatures from direct one-photon photoemission are obtained for any of the photon energies investigated (4.3 eV - 5.1 eV), all below the measured SnS₂ workfunction of 5.2(1) eV [28]. For photon energies up to 4.8 eV, the spectra can be fit well with two overlapping Gaussian features, supported on a linear background to represent the slope of the secondary electron cut-off and with a full-width-half-maximum of ~ 400 meV each (blue and black features in Figure 3a). The two peaks are separated by ~ 300 meV for all photon energies and photoemission angles. The relative intensity of these two features changes as a function of excitation energy, and both features weaken substantially towards higher photon energies. At excitation energies above 4.8 eV, an additional pair of peaks appears at high final state energies, separated by 150 - 200 meV and represented well by Gaussians with a FWHM of ~ 300 meV each (red and brown peaks in Figure 3a).

AR-2PPE simultaneously probes occupied (valence band) and unoccupied (conduction band) levels, either by non-resonant direct absorption of two photons (purple process in Figure 3b) or by excitation and subsequent photoemission from an excited state (orange process in Figure 3b). Spectral features corresponding to photoemission from occupied or unoccupied levels can be differentiated by plotting E_{final} vs. the photon energy. Photoemission from occupied levels requires coherent absorption of two photons and leads to a slope of 2 in a plot of E_{final} vs. , while photoemission from unoccupied levels occurs with a single photon, hence

Figure 3: (Color online) (a) AR-2PPE spectra of SnS₂ for different photon energies, measured at Γ . Solid colored peaks represent Gaussian fits to the observed spectral features after background subtraction. (b) 2PPE cartoon for transitions in SnS₂, illustrating photoemission from an unoccupied level with slope of 1 in a plot of E_{final} vs. $\hbar\omega$ (purple) and photoemission from an occupied level, which would result in a slope of 2 in a plot of E_{final} vs. $\hbar\omega$ (orange). VB, CB: Valence and conduction bands. VL: Vacuum level. (c) Plot of final state energy vs. photon energy for the peaks observed in AR-2PPE of SnS₂. The slopes of ~ 1.0 indicates that all observed peaks correspond to unoccupied levels.

yielding a slope of 1 in such a plot. In both cases, this presumes that in the event that there is no dispersion along , which is a good assumption for layered van der Waals materials such as

SnS₂. We therefore use this distinction to investigate the nature of each of the spectroscopically determined photoemission features in 2PPE of SnS₂. The result of this analysis is shown in Figure 3c: Each experimentally observed peak yields values of $\frac{dE}{d\hbar\omega}$ that are close to 1.0, indicating that all probed levels are unoccupied.

To identify the nature of these spectroscopic features, we measured their dispersion, again averaged over $\overline{\Gamma\text{M}}$ and $\overline{\Gamma\text{K}}$ (Figure 4). The lowest two features are located at 1 - 1.5 eV above E_F , and exhibit a strong upward dispersion. Note that since AR-2PPE generates photoelectrons with low kinetic energies, only the part of the band structure centered around Γ is accessible (see eq. (1)). The HSE level of calculation predicts the magnitude of the indirect fundamental bandgap at 2.31 eV, located between the valence band (VB) edge at Γ and the conduction band (CB) edge at M, consistent with an earlier report [22]. Though the HSE method captures the dispersion and energy offset at the CB minimum correctly, the CB states at other minima such as Γ deviate from the experimental observation. To circumvent this shortcoming and to establish the correlation between the experimental observation and theoretical calculation, a modest upward energy shift of 0.5 eV to match the calculated CB edge at Γ is applied. Consequently, a comparison between the shifted CB at Γ from our computational results and the experimentally observed dispersing band indicates that these spectroscopic features correspond to conduction bands of SnS₂ near Γ . The shift of the calculated bands is necessary to capture the experimental bandgap at Γ of 3.5 eV, which HSE DFT predicts to be 3 eV, and is a consequence of the fact that the absolute conduction band minimum lies at M and not Γ . This is consistent with earlier studies suggesting similar underestimation of the energy offset between the states at the Γ point mainly due to anisotropic self-interaction error correction between the VB and CB states, even at the HSE level of DFT calculation [54–57].

The agreement between theory and experiment is excellent for the dispersion of the lowest band along $\overline{\Gamma\text{M}}$ and $\overline{\Gamma\text{K}}$. A comparison of the theoretical and measured dispersion shows that the conduction band dispersion almost completely coincides along $\overline{\Gamma\text{M}}$ and $\overline{\Gamma\text{K}}$ in the range of $k_{\parallel}$ accessible by AR-2PPE. Moreover, the spin-orbit splitting of a few meV in the conduction band is too small to be experimentally observable in our data. Taken together, the good agreement between theory and experiment validates the computational approach and the

Figure 4: (Color online) Comparison of measured AR-2PPE- peak positions (measured at 10 different photon energies) with the HSE-DFT conduction band structure. Light gray lines are the calculated band structure from Γ to M, while darker grey lines are from Γ to K.

interpretation of the AR-2PPE spectra for this van der Waals layered material.

Both experiment and theory reveal also the existence of a second low-lying and strongly dispersive conduction band, predominantly of Sn 5s character. Computationally, the energy of this band (1.7 eV above E_F at Γ , vs. 1.3 eV in the experiment) is however overestimated in our DFT calculations. We considered several experimental scenarios that might explain this discrepancy: First, an inhomogeneous SnS_2 crystal surface may exhibit two distinct

workfunctions. This would indeed produce “ghost” replica of the conduction band at different energies. Such replica would however be expected for all observed bands with identical energy splitting in AR-2PPE and in principle also in ARUPS, at variance with our experimental results. Second, photoemission from consecutive SnS₂ layers with slightly different electronic structure can also be excluded, since photoemission from a lower layer would *i)* be significantly attenuated due to the limited mean-free path of photoelectrons at this energy, and *ii)* exhibit systematic and strong angle-dependence of the photoemission intensity. This is however not observed, ruling out simple experimental artifacts as the origin of the second conduction band in the experimental spectra.

Instead, the difference may stem from the difficulty of choosing the amount of exact Fock exchange simultaneously appropriate for both occupied and unoccupied levels. This is an artifact of range-separated Hartree-Fock methods like HSE06, where the electron-electron interaction is divided into the short- and long-range contributions to the slowly decaying Fock exchange. The screening parameter included in the electron-electron interaction neglects any environment-, element- or orbital-dependent screening effects during the exchange-correlation energy calculation. This has already been suggested to lead to deviation in the calculated bandgaps from the experimental observation, particularly for states that lie deep within a band [37]. This may be particularly important for SnS₂, since the valence band is predominantly derived from S orbitals, while the conduction band is predominantly derived from Sn orbitals, each with significantly different screening behaviors. Since our HSE calculation relies on the default value of the empirical screening and Hartree-Fock mixing parameters, independent of atomic identity or orbital involved, various combinations of increased screening length and

decreased Hartree-Fock mixing might be needed for a better description of deep-lying energy states [58]. This effect has recently been discussed also in transition metal oxides [37,59,60].

From an experimental point of view, it is also possible that sufficiently S-deficient SnS_2 may develop line-defects that form dispersive bands, offset by a few hundred meV from bulk bands. This has been recently demonstrated in the case of mirror twin boundaries in single layer MoSe_2 [53]. This interpretation is consistent with the existence of a considerable density of S_v invoked in our interpretation of the ARUPS data (Figure 2), albeit for localized bands in the valence band region. Twinning boundaries are certainly present in these SnS_2 crystals, as supported by the observation of stacking faults observed by electron diffraction in bulk 4H- SnS_2 [22].

Further evidence for the important role of defects in the electronic structure of SnS_2 is also obtained directly from the AR-2PPE spectra. As in the ARUPS data, non-dispersive bands are observed also, with two close-lying non-dispersive bands positioned ~ 2.25 eV above E_F . These bands do not correspond to any of the states calculated by DFT, and we tentatively assign them as derived from localized defect states. From Figure 3c it is clear that they are unoccupied bands and only observed over a small energy window in AR-2PPE, implying that they might be resonantly excited from an occupied level. Indeed, the valence band maximum of SnS_2 is non-dispersive and situated at ~ 2.6 eV below E_F , available for resonant excitation to localized excited electronic states at photon energies of 4.9 eV and above. At lower photon energies, this resonance is lost and the states are no longer observed.

4 Conclusions

We present the first experimental momentum-resolved band structure of both ground and excited states in SnS_2 , a quasi-2D layered transition metal dichalcogenide. By a combination of

ARUPS and AR-2PPE we map the valence and conduction bands and identify several defect induced bands. These bands likely arise from ubiquitous sulfur vacancies likely already present in the bulk crystal and possibly further created in the exfoliation and cleaving process. Our data are in good agreement with accurate DFT calculations using the HSE functional, but point also to potential short-comings in the way that exact exchange is treated for conduction band structures. Such insight is enabled by and only available from advanced momentum-resolved spectroscopies such as AR-2PPE, and sets the stage for new developments in electronic structure theory and investigations of ultrafast carrier dynamics at specific points in the band structure. More broadly, the present work lays the foundation for investigations of the electronic structure and dynamics in weakly coupled layered materials and opens avenues towards tailoring their electronic properties.

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