

Many-body signatures of dimensional reduction in quasi-one-dimensional ZrS₃

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The electronic and optical properties of quasi-one-dimensional transition-metal trichalcogenides remain largely unexplored beyond the mean-field approximation, and it is not clear how they evolve as the crystal is thinned. By performing first-principles many-body perturbation theory calculations, we determine the quasiparticle band structures and the polarization-resolved optical response of ZrS₃ in the bulk, bilayer, and monolayer limits, using a hierarchy of methods (hybrid DFT, *GW*, and the Bethe-Salpeter equation). We find that all three systems are indirect-gap semiconductors with a quasidirect character, the direct-indirect splitting being $\delta \approx 0.10\text{--}0.13$ eV and nearly independent of both the level of theory and the dimensionality. The mean-field gaps are almost insensitive to thickness, whereas the quasiparticle corrections increase the gap by ≈ 0.9 eV from bulk to monolayer. The effective exact-exchange fraction reproducing the *GW* gap scales as $\alpha \sim \varepsilon_{\infty}^{-1}$, increasing from ≈ 0.19 to ≈ 0.33 , so that no single hybrid functional describes the full dimensional series. The optical onset blueshifts monotonically ($\approx 2.4 \rightarrow 2.8 \rightarrow 3.0$ eV) and the near-edge absorption is strongly dichroic. A change in light polarization does not simply shift the excitonic resonance (≈ 0.09 eV); it also reorganizes the underlying excitonic wave function, selecting distinct band channels and **k**-space regions. A real-space, participation-ratio analysis resolves moderately delocalized, Wannier-Mott-like excitons templated along the covalent chains. They are predominantly sulfur-derived (75%–88% of the density on sulfur for the chain-polarized bulk states), which identifies them as (S₂)^{2−} disulfide excitations rather than S $\rightarrow$ Zr charge-transfer states, while in the bilayer the electron delocalizes across both layers, the real-space imprint of interlayer screening. These results provide a consistent reference for the quasiparticle and excitonic energy scales of ZrS₃ from the bulk to the few-layer limit.

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I. INTRODUCTION

Low-symmetry van der Waals semiconductors provide a promising route to electronic and optical responses that are difficult to achieve in high-symmetry layered materials. Transition-metal trichalcogenides, MX₃, are especially useful in this context because they combine weak interlayer bonding with a highly anisotropic in-plane structural network. Unlike many transition-metal dichalcogenides, whose individual layers are nearly isotropic within the basal plane, MX₃ layers consist of quasi-one-dimensional structural units. As a result, these materials exhibit strongly direction-dependent lattice dynamics, carrier transport, and optical selection rules [1,2]. Zirconium trisulfide, ZrS₃, is a representative example of this family. It crystallizes in the monoclinic *P*2₁/*m* phase, where distorted ZrS₆ trigonal-prismatic units connect into chains along the crystallographic *b* axis, while adjacent layers are separated by van der Waals gaps [3–5]. This bulk structure, illustrated in Fig. 1, places ZrS₃ between conventional

two-dimensional semiconductors and truly one-dimensional systems: Although the material is layered and exfoliable, its electronic and optical behavior remains strongly governed by the chain direction [6].

Despite this seemingly simple structural picture, the fundamental electronic and optical gaps of ZrS₃ remain difficult to define unambiguously from the available literature. Most experimental gap estimates are optical in nature, whereas a direct benchmark for the quasiparticle gap is still lacking. Angle-resolved photoemission and nanoARPES measurements have provided valuable information on the occupied valence-band dispersion of bulk ZrS₃, but they cannot determine the full quasiparticle gap because the unoccupied conduction-band minimum is not accessed. In particular, nanoARPES places the valence-band maximum at Γ , approximately 1.9 eV below the Fermi level in strongly *n*-type ZrS₃(001) samples; however, this energy corresponds to $E_F - E_{\text{VBM}}$, not to the fundamental quasiparticle gap $E_{\text{CBM}} - E_{\text{VBM}}$ [7]. A direct experimental determination of the quasiparticle gap would instead require probes of the unoccupied electronic structure, such as inverse photoemission, scanning tunneling spectroscopy, or pump-probe photoemission [8].

The optical response of ZrS₃ has likewise been interpreted in different ways over the years. Early absorption measurements on bulk crystals revealed a pronounced dichroic absorption edge and assigned an optical band gap of about 2.8 eV to ZrS₃ [4]. Subsequent low-temperature absorption

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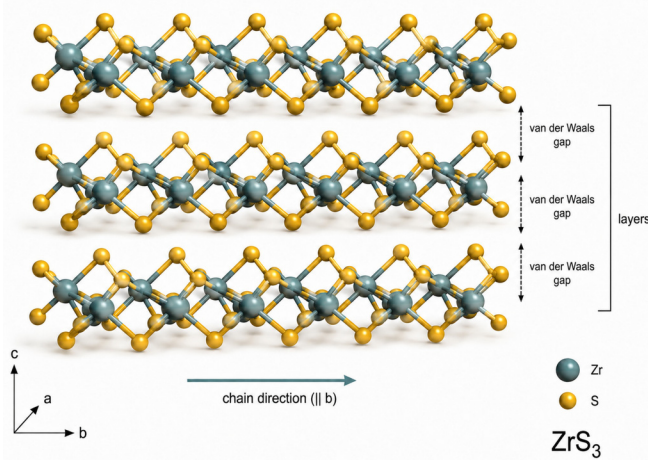


FIG. 1. Sketch of bulk ZrS₃, highlighting the quasi-one-dimensional chains running along the crystallographic *b* direction and the van der Waals gaps between adjacent layers.

experiments refined this assignment, identifying indirect optical gaps of 2.055 eV for light polarized parallel to the chain direction, $E \parallel b$, and 2.085 eV for perpendicular polarization, $E \perp b$ [9]. A later reflection study combined with Kramers-Kronig analysis showed that the dominant low-temperature spectral feature near the band edge is not the quasiparticle gap itself, but a sharp excitonic absorption band at 2.573 eV for $E \parallel b$, attributed to a direct allowed transition; a weaker absorption band was also reported at 2.441 eV [10]. More recently, measurements on thin ZrS₃ films found an indirect optical gap of 1.81 eV, while polarized microphotoluminescence and time-resolved spectroscopy on multilayer quasi-one-dimensional ZrS₃ nanoribbons revealed excitonic emission features in the 1.9–2.2 eV range, supporting a quasi-direct band-edge character [11,12]. Thus, the experimentally relevant quantities for comparison with Bethe-Salpeter calculations are optical transition energies: the indirect bulk optical edge around 2.0 eV, the bright excitonic transition at 2.573 eV for $E \parallel b$, and the lower-energy multilayer excitonic features near 1.9 to 2.2 eV. None of these energies, however, should be interpreted as a direct experimental benchmark for the quasiparticle gap entering a GW calculation.

The theoretical picture is similarly fragmented. Density-functional and hybrid-functional studies consistently describe ZrS₃ as a semiconductor with pronounced anisotropy between the chain direction and the transverse in-plane direction. Nevertheless, the predicted gap depends sensitively on the level of theory, dimensionality, structural relaxation, and treatment of dielectric screening. For the isolated monolayer, previous calculations reported an indirect HSE06 gap close to 1.9 eV and a nearly direct band-edge structure, with the direct transition at Γ lying only slightly above the fundamental indirect gap [2,13]. Broader first-principles surveys of group-IV transition-metal trichalcogenides have also highlighted their low cleavage energies, strongly anisotropic carrier transport, and potential for reduced-dimensional optoelectronic applications, particularly in TiS₃, ZrS₃, and related compounds [1,2]. At the many-body level, existing G_0W_0 and Bethe-Salpeter studies of MX₃ systems have provided important insight into

quasiparticle corrections and optical absorption. However, ZrS₃ has mostly been treated as part of broader materials surveys, and a systematic, internally consistent comparison of bulk, monolayer (1L), and bilayer (2L) ZrS₃ within the same structural, quasiparticle, and excitonic workflow is still missing [14]. This leaves unresolved a central question: How the fundamental quasiparticle gap, the lowest optically active excitation, and the electron-hole binding energy evolve as ZrS₃ is reduced from the bulk crystal to the few-layer limit.

This issue is not only fundamental, but also directly relevant for device design. The coexistence of a visible-range optical gap, strong in-plane anisotropy, quasi-one-dimensional band-edge states, and van der Waals exfoliability makes ZrS₃ a promising platform for polarization-sensitive optoelectronics. Angle-resolved photoluminescence experiments have demonstrated strongly dichroic emission, with an enhanced optical response for electric fields aligned with the structural chains. This behavior points to possible applications in linearly polarized photodetectors, anisotropic light emitters, near-field imaging, and optical communication [15]. Related anisotropic excitonic effects have been exploited in multilayer ZrS₃ nanoribbons and in p-GaSe/n-ZrS₃ heterojunctions, where an axially polarized photovoltaic response was observed [12]. From a first-principles perspective, ZrS₃-based type-II van der Waals heterobilayers, including ZrS₃/MS₂ and ZrS₃/MX_Y systems, have been proposed as candidates for ultrathin excitonic solar cells because of their favorable band alignment, strong absorption, and spatial separation of photoexcited carriers [16]. More recent ZrS₃/MoS₂ heterostructure devices further underline the potential of this material family for high-performance linearly polarized photodetection [17]. A predictive description of quasiparticle and excitonic energy scales is therefore essential both for interpreting existing optical spectra and for guiding the design of ZrS₃-based photovoltaic, photodetecting, and polarization-selective devices.

In this work, we address these issues by investigating the electronic and optical properties of bulk, monolayer, and bilayer ZrS₃ within a unified many-body perturbation-theory framework. Starting from first-principles ground-state calculations, we compute the quasiparticle band structures using the GW approximation and the neutral excitation spectra by solving the Bethe-Salpeter equation. This approach allows us to distinguish, on equal footing, the fundamental quasiparticle gap from the lowest optical excitation, determine the direct or indirect character of the relevant transitions, quantify the electron-hole binding energy, and analyze the dimensional evolution of the optical anisotropy. By comparing the calculated BSE spectra with experimentally measured optical edges and excitonic peaks, while avoiding the common identification of optical transition energies with quasiparticle gaps, we provide a consistent reference for the band-gap and excitonic physics of ZrS₃ from the bulk to the few-layer limit.

II. COMPUTATIONAL DETAILS

The initial atomic structure of bulk ZrS₃ was taken from the experimental crystallographic refinement of Furuseth, Brattås, and Kjekshus, who determined the monoclinic ZrSe₃-type structure of zirconium trisulfide from single-crystal x-ray

diffraction data [3]. The experimental lattice parameters and internal coordinates were subsequently relaxed at the hybrid density-functional level using the periodic Gaussian-orbital code CRYSTAL23 [18,19]. Geometry optimizations were carried out with the PBE0 exchange-correlation functional [20], supplemented by Grimme's D3 dispersion correction [21], and triple- ζ valence plus polarization Gaussian basis sets of the pob-TZVP family, including basis functions specifically optimized for crystalline main-group and fifth-period elements [22,23]. Long-range correlation is essential in a layered compound such as ZrS_3 , and its effect is confined to the stacking coordinate (see Supplemental Material [24]). The Coulomb and exchange lattice sums were screened using TOLINTEG 10 10 10 16 32 in all CRYSTAL23 calculations. For the exchange series, these values correspond to $T_s = 10$, $T_g = 16$, and $T_q = 32$, thus satisfying the conservative relation $T_q = 2T_g$ [25]. Previous studies have reported that PBE0 outperforms PBE in describing both the structural parameters and the single-particle electron density [26,27]. Brillouin-zone integrations for the bulk optimization employed an $4 \times 6 \times 2$ Monkhorst-Pack mesh [28], and the self-consistent-field cycle was converged until the total-energy variation was smaller than 10^{-9} a.u.

Starting from the PBE0-optimized bulk structure, isolated one-layer and two-layer ZrS_3 systems were constructed using the SLAB procedure implemented in CRYSTAL23. This construction preserves the two-dimensional periodicity of the ZrS_3 sheets while removing the three-dimensional periodic stacking of the bulk crystal. Due to the slab-generation convention adopted in CRYSTAL23, the in-plane a and b axes of the few-layer systems are interchanged with respect to the crystallographic setting used for the bulk phase; this convention is explicitly taken into account in the analysis and presentation of the results. The resulting 1L and 2L structures were fully relaxed at the same PBE0/pob-TZVP level of theory. For the optimized bulk, monolayer, and bilayer geometries, hybrid-functional electronic band structures were computed within the generalized Kohn-Sham framework using PBE0 [20], the Coulomb-attenuating CAM-B3LYP functional [29], and the screened-exchange HSE06 functional [30–32], always employing the same Gaussian basis-set representation. The PBE0-optimized structures obtained with CRYSTAL23 were then used as structural input for plane-wave density-functional calculations performed with the QUANTUM ESPRESSO distribution [33–35]. In this step, the exchange-correlation energy was described within the Perdew-Burke-Ernzerhof generalized-gradient approximation [36]. The electron-ion interaction was treated using optimized norm-conserving pseudopotentials from the PSEUDODOJO library [37], and the Kohn-Sham wave functions were expanded in a plane-wave basis with a kinetic-energy cutoff of 110 Ry. Self-consistent calculations were converged to an energy threshold of 10^{-9} a.u. The Brillouin zone was sampled using a $4 \times 6 \times 2$ mesh for bulk ZrS_3 , while $6 \times 4 \times 1$ meshes were adopted for the 1L and 2L slab geometries, consistently with their reduced dimensionality. For the 1L and 2L slab geometries, a vacuum region of approximately 20 Å was introduced along the nonperiodic direction in order to prevent spurious interactions between periodic replicas, and the long-range Coulomb interaction was truncated along z following the two-dimensional truncation

scheme of Sohler, Calandra, and Mauri [38]. Starting from the converged SCF wave functions, denser k -point meshes with an increased number of electronic bands were generated through subsequent non-self-consistent-field (NSCF) calculations. All calculations were performed including long-range dispersion interactions through Grimme's DFT-D3 correction [21]. The PBE wave functions obtained from QUANTUM ESPRESSO were used as the mean-field starting point for the many-body perturbation-theory calculations performed with the BERKELEYGW package [39]. Quasiparticle corrections were evaluated within the GW approximation, with the frequency dependence of the screened Coulomb interaction described through the generalized plasmon-pole model of Hybertsen and Louie [40]. For each system considered in this work, namely bulk, monolayer, and bilayer ZrS_3 , all parameters entering the quasiparticle and optical calculations were independently converged. Consistently with the mean-field treatment, the same truncation of the Coulomb interaction along the nonperiodic direction was enforced throughout the GW and BSE calculations for the 1L and 2L systems, using the slab-truncation scheme of Ismail-Beigi [41], in order to eliminate spurious interactions between periodic replicas of the slab. The use of PBE as the mean-field reference, while the geometries and the hybrid band structures rest on PBE0, requires a comment: At the single-shot G_0W_0 level the quasiparticle spectrum retains a memory of the underlying mean-field gap through the screening [42]. A PBE0 reference could not be inherited from the hybrid calculations, which were performed with localized Gaussian orbitals in CRYSTAL23, whereas BERKELEYGW uses plane-wave-based wave functions, and repeating them in the plane-wave framework for the three systems would have been computationally prohibitive. We have therefore gone beyond the single-shot approximation rather than beyond the semilocal starting point. An eigenvalue self-consistency cycle was performed at the G_iW_i level for each dimensionality, the quasiparticle energies entering both G_i and W_i being updated at every iteration [42,43], and quasiparticle corrections were computed explicitly for all bands included in the many-body calculation, without introducing scissorlike rigid shifts or extrapolated band corrections. The quasiparticle gaps converge after three cycles (see Supplemental Material [24]), so that the reported energies correspond to a converged fixed point of the scheme rather than to the first perturbative correction to the PBE spectrum, and the dependence on the PBE eigenvalue spectrum is largely removed. Eigenvalue self-consistency is not, however, a formal guarantee of starting-point independence, since the quasiparticle wave functions remain frozen at their PBE form [43]. In ZrS_3 the residual is expected to be small: PBE and the hybrid functionals return the same band ordering and the same near-edge topology, the effect of exact exchange being a renormalization of the gap rather than a reconstruction of the frontier manifold, and the pathologies that make starting-point effects severe—a metallic state, an inverted band ordering, a qualitatively incorrect orbital hybridization [42]—do not occur here. The results are accordingly labeled throughout as eigenvalue-self-consistent $G_iW_i@PBE$ and $G_iW_i@PBE-BSE$. The optical absorption spectra were subsequently obtained by solving the Bethe-Salpeter equation for the correlated electron-hole two-particle

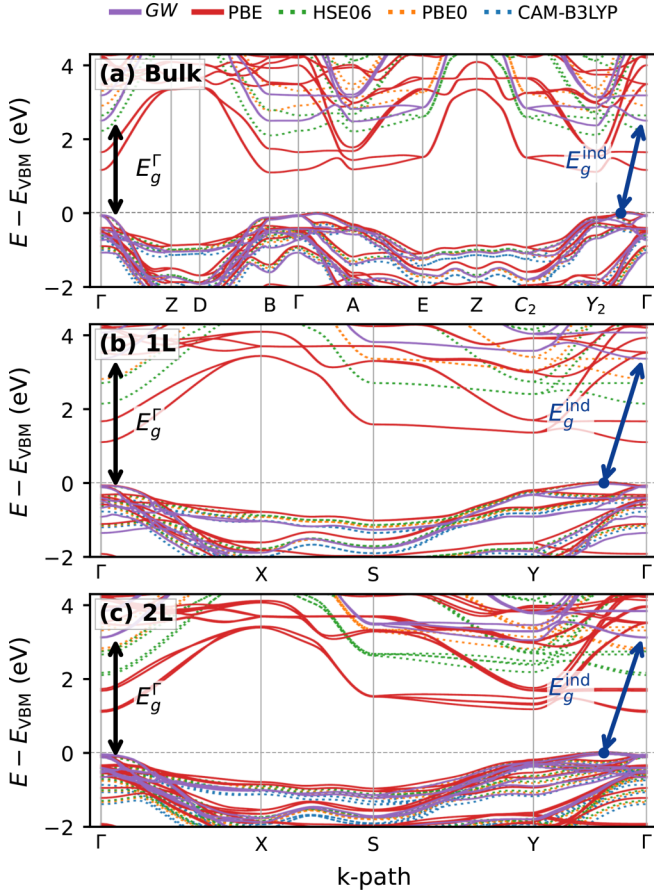


FIG. 2. Band structures of (a) bulk, (b) monolayer (1L), and (c) bilayer (2L) ZrS_3 along the high-symmetry paths, computed within GW (purple), PBE (red), and the hybrid functionals HSE06, PBE0, and CAM-B3LYP, shown as dotted curves. Energies are referenced to the VBM. The vertical black arrow marks the direct GW gap at Γ (E_g^Γ), while the blue arrow denotes the indirect GW gap (E_g^{ind}), connecting the off- Γ VBM to the CBM at Γ .

Hamiltonian. For the excitonic calculations, Brillouin-zone samplings denser than those used to converge the GW quasi-particle corrections were employed, in order to resolve both the electron-hole interaction kernel and the low-energy excitonic structure with sufficient accuracy. Spin-orbit coupling was not included in the calculations (see Supplemental Material [24] for more details). The final values adopted for the dielectric-matrix cutoffs, number of empty states, quasiparticle band windows, Coulomb-interaction treatment, number of $G_i W_i$ cycles, and coarse and fine k -point meshes are reported in the Supplemental Material [24], together with the corresponding convergence tests and the optimized structures.

III. RESULTS

Figure 2 displays the electronic band structures of bulk, monolayer (1L), and bilayer (2L) ZrS_3 obtained within PBE, the hybrid functionals HSE06, PBE0, and CAM-B3LYP, and the GW approximation. The PBE dispersion has been obtained by means QE, the hybrid ones using CRYSTAL23 while the latter with BERKELEYGW. The corresponding direct and

TABLE I. Direct gap at Γ , E_g^Γ , and fundamental indirect gap, E_g^{ind} (CBM at Γ , VBM slightly off Γ), of bulk, monolayer (1L) and bilayer (2L) ZrS_3 at the GW, PBE, HSE06, PBE0, and CAM-B3LYP levels (eV).

Sys.	Gap	GW	PBE	HSE06	PBE0	CAM
Bulk	E_g^Γ	2.567	1.246	2.306	2.978	5.194
	E_g^{ind}	2.462	1.120	2.197	2.863	4.974
1L	E_g^Γ	3.445	1.205	2.216	2.878	4.914
	E_g^{ind}	3.325	1.085	2.111	2.768	4.804
2L	E_g^Γ	3.208	1.188	2.209	2.918	4.941
	E_g^{ind}	3.085	1.060	2.085	2.803	4.824

fundamental gaps are reported in Table I. In the bulk, ZrS_3 crystallizes in the monoclinic $P2_1/m$ structure as a stacking of ZrS_6 trigonal-prismatic chains, each containing a short S-S dimer. This bonding motif establishes a clear hierarchy of energy scales: Strong intrachain Zr-S and S-S covalency coexists with much weaker interchain and interlayer, van der Waals-like coupling. As a consequence, the low-energy electronic structure acquires a marked quasi-one-dimensional character.

In the bulk setting, the chains define the light-mass, strongly dispersive direction and run along the crystallographic b axis (≈ 3.59 Å). The monolayer and bilayer geometries were generated from the bulk using the SLAB option of CRYSTAL23, which takes the surface normal as the nonperiodic c direction and accordingly relabels the in-plane lattice vectors. In the slab cells, the same physical chain direction is therefore mapped onto the a axis. Thus, the quasi-one-dimensional direction is denoted by b in the bulk and by a in the few-layer systems, although it corresponds to the same structural motif. In all cases, the dispersion perpendicular to the chains remains comparatively weak.

At all levels of theory considered here, the fundamental gap is indirect. The conduction-band minimum (CBM) is located at Γ , whereas the valence-band maximum (VBM) is slightly displaced away from Γ . The orbital-projected density of states, reported in the Supplemental Material [24], shows that the frontier manifold on both sides of the gap is dominated by sulfur s and p states, with only a minor admixture of Zr $4d$ character. This strong sulfur weight, associated with the S-S dimers, indicates that the fundamental transition is primarily intrasulfur in character rather than a conventional $\text{S} \rightarrow \text{Zr}$ charge-transfer excitation. The resulting band dispersion is highly anisotropic: It is steep along the chain direction, namely b in the bulk and a in the slabs, and nearly flat in the transverse directions. This is consistent with the quasi-one-dimensional connectivity of the ZrS_6 prisms and with the anisotropic valence dispersion observed by nanoARPES [7].

A first point concerns the topology of the near-edge bands, which should be distinguished from the absolute value of the gap. The direct-indirect splitting $\delta = E_g^\Gamma - E_g^{\text{ind}}$ remains nearly unchanged across dimensionalities and exchange-correlation treatments, with $\delta \approx 0.10$ – 0.13 eV for all three systems and all five methods, apart from the bulk CAM-B3LYP value of 0.22 eV. Since δ measures the energy separation between the valence maximum at Γ and the true off- Γ VBM, this near invariance shows that the location and

curvature of the valence extrema are primarily fixed by the one-particle hopping topology of the chains. They are not substantially reorganized by either hybrid exchange or the GW self-energy.

Equivalently, the hybrid-functional and quasiparticle corrections act on the frontier bands largely as a scissorlike renormalization: They modify the size of the gap while leaving the underlying dispersion almost unchanged. The indirect character, the quasidirect nature of the gap, and the effective-mass anisotropy are therefore robust consequences of the crystal and bonding topology. By contrast, the magnitude of the gap is the quantity that is sensitive to the treatment of exchange and correlation.

The gap magnitude exhibits a much stronger dependence on the electronic-structure approximation. PBE yields fundamental gaps of only ~ 1.1 – 1.2 eV, as expected from the absence of the derivative discontinuity in the Kohn-Sham potential and from residual self-interaction. Introducing non-local Fock exchange opens the gap in a manner controlled by the amount and range of exact exchange. HSE06, where the long-range part of the Coulomb interaction is screened, gives gaps of ~ 2.1 – 2.3 eV. PBE0, with a global 25% fraction of exact exchange, increases them to ~ 2.8 – 3.0 eV. CAM-B3LYP gives substantially larger values, ~ 4.8 – 5.2 eV, because its long-range exact-exchange fraction rises to approximately 65%.

This ordering has a direct physical interpretation. In an extended polarizable solid, the bare Fock interaction is screened by the macroscopic electronic dielectric response, characterized by ϵ_∞ . HSE06 partially mimics this effect by truncating exact exchange at long range, whereas PBE0 retains a fixed unscreened fraction at all distances. CAM-B3LYP enhances precisely the long-range component that should instead be suppressed by dielectric screening. Since CAM-B3LYP is parametrized for finite molecular systems, where the asymptotic dielectric constant is effectively unity, its large gaps should be regarded here as nontransferable upper bounds rather than physical quasiparticle gaps.

The thickness dependence separates the mean-field and many-body descriptions. At the mean-field level, the gap is nearly insensitive to dimensionality. The PBE, HSE06, and PBE0 gaps change by less than ~ 0.1 eV between bulk, bilayer, and monolayer, with no systematic trend. This weak variation reflects the fact that a fixed fraction of exact exchange does not respond to the changing dielectric environment.

The GW gaps behave qualitatively differently. Both the direct and indirect quasiparticle gaps increase monotonically as the system is thinned: $E_g^\Gamma = 2.57 \rightarrow 3.21 \rightarrow 3.45$ eV and $E_g^{\text{ind}} = 2.46 \rightarrow 3.09 \rightarrow 3.33$ eV for bulk $\rightarrow$ 2L $\rightarrow$ 1L. The quasiparticle correction relative to PBE, $\Delta\Sigma = E_g^{\text{GW}} - E_g^{\text{PBE}}$, correspondingly increases from 1.34 eV in the bulk to 2.02 eV in the bilayer and 2.24 eV in the monolayer, as summarized in Table II. Thus, upon isolating a single layer, the self-energy correction almost doubles.

This behavior is the expected many-body signature of reduced dielectric screening in low-dimensional systems. As the electronic screening is weakened, the screened Coulomb interaction W becomes less screened, and the GW self-energy

TABLE II. Dimensional and many-body trends in the fundamental (indirect) gap, ordered by decreasing dimensionality: the GW gap E_g^{ind} , the self-energy correction over PBE $\Delta\Sigma = E_g^{\text{GW}} - E_g^{\text{PBE}}$, the dimensional opening relative to the bulk $\delta_{\text{dim}} = E_g^{\text{GW}} - E_g^{\text{GW}}(\text{bulk})$, and the effective global exact-exchange fraction α_{eff} reproducing the GW gap under a linear PBE–PBE0 interpolation. Energies in eV.

System	E_g^{ind}	$\Delta\Sigma$	δ_{dim}	α_{eff}
Bulk	2.462	1.342	0.000	0.19
2L	3.085	2.025	0.623	0.29
1L	3.325	2.240	0.863	0.33

$\Sigma = i\text{GW}$ produces a larger quasiparticle correction. This mechanism is absent in the mean-field schemes considered above, which are not explicitly sensitive to the thickness-dependent dielectric response. The same physics is reflected in the crossover between hybrid-functional and GW gaps. In the bulk, the GW gap lies between the HSE06 and PBE0 values. In the bilayer and monolayer, however, it exceeds PBE0 by 0.28 and 0.56 eV, respectively.

This trend can be quantified by introducing an effective global Fock fraction α_{eff} , defined as the value that reproduces the GW gap through a linear interpolation between PBE and PBE0. As shown in Table II, α_{eff} increases from 0.19 in the bulk to 0.29 in the bilayer and 0.33 in the monolayer. The bulk value lies within the usual range of global hybrid functionals, whereas the few-layer values exceed a standard 25% mixing. Since the optimal fraction in a dielectric-dependent hybrid is expected to scale approximately as $\alpha_{\text{opt}} \sim \epsilon_\infty^{-1}$, the monotonic increase of α_{eff} provides a direct fingerprint of the reduction of electronic screening from bulk to monolayer. It also demonstrates that no single, system-independent hybrid functional can reproduce the gap across all dimensionalities.

The bilayer occupies an intermediate position in this screening hierarchy. Its GW gap is substantially closer to the monolayer value than to the bulk value. Of the total 0.86 eV increase in the indirect gap from bulk to monolayer, the bilayer already accounts for 0.62 eV, corresponding to approximately 72% of the full opening. This rapid evolution shows that the self-energy is governed mainly by the immediate dielectric environment: The addition of one neighboring layer restores a large fraction, though not all, of the bulk screening. Full convergence to the three-dimensional limit is therefore expected to be relatively slow.

It is important to distinguish this dielectric interlayer effect from ordinary one-particle interlayer hybridization. The reduction of the bilayer quasiparticle gap relative to the monolayer is not a band-hybridization effect. It is instead a screening effect: The enhanced polarizability of the thicker slab renormalizes the quasiparticle energies through the self-energy.

These results can be compared with the existing first-principles literature on ZrS_3 , which has so far been almost entirely limited to mean-field calculations. At the hybrid-functional level, our gaps are consistent with previous HSE06 results. Reported indirect gaps are 1.87 eV for the bulk and 1.92–1.93 eV for the monolayer [13,44], compared with our values of 2.20 and 2.11 eV, respectively. The residual

~ 0.2 – 0.3 eV upward shift is systematic but does not imply a different physical picture. We attribute it mainly to the localized all-electron TZVP basis and to details of the hybrid-functional implementation, with possible secondary contributions from the relaxed lattice parameters.

The near-edge band topology is also consistent with previous work. Mortazavi *et al.* find the CBM at Γ and the VBM displaced away from Γ , with a direct-indirect splitting of only ~ 0.08 eV [13], in close agreement with our δ . Similarly, the strain-induced indirect-to-direct transition predicted for the monolayer [2] can be understood as a consequence of the near degeneracy between the Γ and off- Γ valence extrema. This is the same microscopic feature underlying the quasidirect assignment in the present work. The nanoARPES measurements of Ref. [7] further support this interpretation by showing an anisotropic, quasi-one-dimensional valence manifold.

The comparison with the literature also emphasizes the central result of the present analysis. At the mean-field level, the weak thickness dependence found here mirrors previous HSE06 calculations: The reported bulk and monolayer gaps differ by only ~ 0.05 eV [2]. The large dimensional renormalization reported here is therefore intrinsically a *GW* effect and lies beyond the scope of semilocal or hybrid mean-field treatments. Quasiparticle corrections of similar magnitude have been reported in earlier *GW*-BSE studies of the broader MX_3 family [14]. To our knowledge, however, a systematic bulk-to-bilayer-to-monolayer quasiparticle comparison for ZrS_3 has not previously been reported.

Taken together, bulk, bilayer, and monolayer ZrS_3 form a well-defined dielectric screening ladder. The near-edge band topology is essentially invariant: The gap remains indirect but quasidirect, and the frontier bands retain their strongly anisotropic character. The mean-field gap is likewise nearly independent of thickness. In contrast, the quasiparticle gap increases monotonically along bulk $\rightarrow$ 2L $\rightarrow$ 1L, tracking the reduction of dielectric screening through a self-energy correction that grows from 1.3 to 2.2 eV. The fundamental gap of few-layer ZrS_3 is therefore controlled primarily by the dimensionality of the dielectric response, rather than by a substantial reconstruction of the underlying one-particle bands. A quantitative description of this gap consequently requires an explicit many-body treatment, rather than a transferable hybrid-functional parametrization calibrated at the bulk level.

Figure 3 collects the polarization-resolved absorption (just in the energy window around the first peak, to have a direct comparison with the corresponding experimental first peak) of the three systems for light polarized parallel ($\parallel$) and perpendicular ($\perp$) to the quasi-one-dimensional (q1D) Zr-S chains in each cell—the crystallographic b axis in the bulk, relabeled a in the slab cells—and the fitted maxima are listed in Table III. Two robust trends organize the spectra. First, the optical onset blueshifts monotonically with reduced dimensionality, the first peak moving from ~ 2.4 – 2.6 eV in the bulk to ~ 2.8 eV in the bilayer and ~ 3.0 – 3.1 eV in the monolayer. This is the optical fingerprint of the many-body, screening-driven opening of the quasiparticle gap upon exfoliation: The mean-field gaps are nearly dimension-independent, and it is only the self-energy—through the collapse of the dielectric screening in the 2D limit—that drives the blueshift, in line with the quasiparticle gaps of the preceding section.

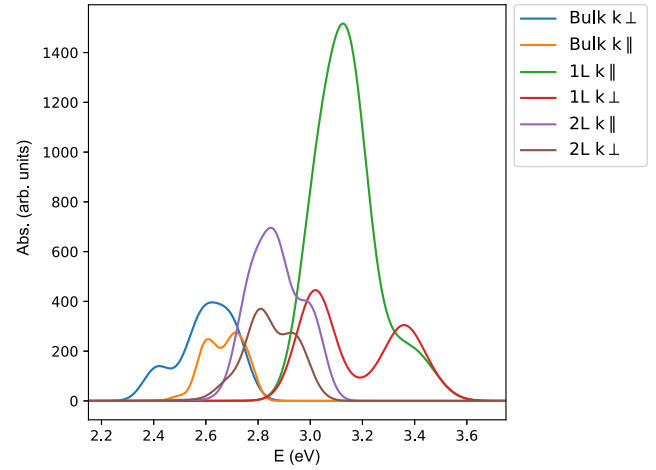


FIG. 3. Polarization-resolved near-edge absorption of bulk, monolayer (1L), and bilayer (2L) ZrS_3 for light polarized parallel ($\parallel$) and perpendicular ($\perp$) to the q1D chain axis (common arbitrary-unit scale). Peak maxima are tabulated in Table III.

Second, we restrict the analysis to the lowest-energy bright peak, so as to compare directly with the first experimental exciton. This reveals a near-edge linear dichroism aligned with the chain axis in all systems: The fundamental bright exciton is polarized along the chains from the bulk to the monolayer. In the bulk this first peak is not an isolated maximum but a faint shoulder on the low-energy flank of the dominant band, it is located at 2.40 eV for $e \perp b$ and at 2.60 eV for $e \parallel b$, with the chain component the stronger of the two by $A_{\parallel}/A_{\perp} \simeq 2.1$ in peak height. In the slabs the first peak coincides with the dominant near-edge maximum and the chain polarity is more pronounced still, $A_{\parallel}/A_{\perp} \simeq 3.4$ in the monolayer and $\simeq 1.9$ in the bilayer. The effect is largest in the monolayer, whose chain-polarized first peak is the most intense feature of the whole set. This uniformly chain-polarized lowest bright peak corresponds to the sharp, strongly $e \parallel b$ direct exciton resolved in low-temperature

TABLE III. First-peak absorption maxima extracted from Fig. 3. Polarization is given both geometrically ($\parallel/\perp$ to the chains) and as the crystallographic field direction. E_{peak} is the position of the *first* (lowest-energy) resolved peak of each spectrum—obtained by a Gaussian deconvolution of the near-edge feature where this peak is not isolated, as in the bulk, where it survives only as a weak shoulder on the low-energy flank of the dominant near-edge band; A_{peak} is the corresponding peak height (arb. units, common scale, normalized to the strongest first peak). $E_s^{(1)}$ is the energy of the lowest bright BSE state feeding each band (see Table IV).

System	Pol.	E_{peak} (eV)	A_{peak}	$E_s^{(1)}$ (eV)
Bulk	$\perp$ ($e \parallel a$)	2.40	0.07	2.409
Bulk	$\parallel$ ($e \parallel b$)	2.60	0.15	2.491
1L	$\parallel$ ($e \parallel a$)	3.12	1.00	3.028
1L	$\perp$ ($e \parallel b$)	3.02	0.29	3.015
2L	$\parallel$ ($e \parallel a$)	2.85	0.45	2.746
2L	$\perp$ ($e \parallel b$)	2.82	0.24	2.686

TABLE IV. Reciprocal-space microscopic summary of the first bright exciton of each system and polarization. E_S is the BSE energy; “leading channels” lists the dominant $v \rightarrow c$ contributions (% of the norm); $\mathbf{k}$ -character distinguishes Γ -centered from zone-edge (ZE) states (a and b are crystallographic, with the chain along b in the bulk and along a in 1L/2L). The complementary real-space (Voronoi and participation-ratio) descriptors of the same excitons are collected in Table V.

System	Pol.	E_S (eV)	Leading channels	$\mathbf{k}$ -character
Bulk	$\parallel (b)$	2.491	v_1c_1 (99)	ZE: (0.5, ± 0.04 , 0)
Bulk	$\perp (a)$	2.409	v_1c_1 (84%), v_2c_1 (15)	ZE: (0.5, 0, 0) + Γ
1L	$\parallel (a)$	3.028	v_1c_2 (38%), v_2c_1 (30%), v_1c_1 (11)	ZE along b^*
1L	$\perp (b)$	3.015	v_4c_1 (30%), v_3c_1 (27%), v_2c_1 (26)	Γ -centered
2L	$\parallel (a)$	2.746	v_1c_1 (33%), v_2c_1 (18%), v_1c_2 (11)	ZE along b^* ; $k_a \simeq 0$
2L	$\perp (b)$	2.686	v_1c_1 (21%), v_2c_2 (21%), v_4c_2 (11)	Γ -centered

strain-free crystals [4,10]. In the bulk the lowest bright state is the transverse one ($E_S^{(1)} = 2.409$ eV), so the more intense chain-polarized first peak sits just above it, and the apparent polarity of the dichroism is energy-resolved, as detailed below.

These energy and intensity trends are not the only manifestation of the anisotropy of ZrS_3 : The polarization of the exciting field does not merely shift the exciton energy, it selects different correlated states. As summarized in Table IV (the full $\mathbf{k}$ -resolved fat-band maps of each eigenvector are given in the Supplemental Material [24]), the chain-parallel and chain-perpendicular excitons of the same system differ both in the band channels they are built from and in the region of the Brillouin zone they sample. In the *bulk*, both bright excitons are sharply valley-selective and reside at the Brillouin-zone (BZ) boundary rather than at Γ . The chain-parallel (b) state is essentially monoconfigurational, with 99% of its weight on the single $v_1 \rightarrow c_1$ channel, and is concentrated in two symmetry-related pockets at (0.5, ± 0.042 , 0) that already exhaust $\sim 87\%$ of its norm; the direct Γ contribution is negligible (0.3%). The transverse (a) state is a two-channel near-gap superposition, $v_1 \rightarrow c_1$ (84%) and $v_2 \rightarrow c_1$ (15%), peaked at the zone edge (0.5, 0, 0) with a sizable but secondary Γ admixture (7%). Thus, even in the bulk, the lowest dipole-allowed excitations are not Γ -point transitions but zone-edge excitons, consistent with the indirect, quasidirect character ($\delta \approx 0.10$ – 0.13 eV) established for the single-particle gap.

Reducing the dimensionality redistributes the spectral weight over several band pairs. In the monolayer, the chain-longitudinal (a) exciton is a multiband superposition within the $(v_1, v_2) \rightarrow (c_1, c_2)$ manifold, the leading channels being $v_1 \rightarrow c_2$ (38%) and $v_2 \rightarrow c_1$ (30%); its weight is tightly confined along the chain reciprocal axis ($|k_a| \leq 0.071$ holds 88%) yet displaced to the transverse zone edge b^* . The transverse (b^*) monolayer exciton, in contrast, has an almost pure single-conduction electron (96% on c_1) dressed by a multiband valence hole (v_2, v_3, v_4 each ~ 27 – 30%) and is Γ -centered (91% within $|k_a| \leq 0.071$), in keeping with the zone-center valence-band maximum seen by nanoARPES [7].

The spatial structure of each BSE exciton is analyzed from the conditional electron density $\rho_S(\mathbf{r}_e; \mathbf{r}_h) = |\Psi_S(\mathbf{r}_e, \mathbf{r}_h)|^2$, obtained by fixing the hole at a selected atomic site. The electron-hole separation is quantified through the directional root-mean-square radii R_a , R_b , and R_c , obtained by projecting

$\mathbf{r}_e - \mathbf{r}_h$ along the crystallographic axes a , b , and c , respectively. The total excitonic radius

$$R_{\text{exc}} = \sqrt{\langle |\mathbf{r}_e - \mathbf{r}_h|^2 \rangle}$$

measures the overall RMS electron-hole distance, while r_{90} denotes the radius enclosing 90% of the conditional electron density around the fixed hole. Periodic boundary conditions are treated through a minimum-image convention. The effective number of primitive cells involved in the excitation, $N_{\text{cell}}^{\text{eff}}$, is obtained from the real-space participation ratio and provides a measure of exciton delocalization. The quantities Z16% and Z40% are obtained from a Voronoi decomposition of the density and give the percentage of the excitonic electron density assigned to atomic domains with nuclear charge $Z = 16$ and $Z = 40$, i.e., S and Zr in ZrS_3 . Finally, $Q_a^{\text{xy}}\%$ and $Q_b^{\text{xy}}\%$ quantify the fraction of the in-plane density associated with the crystallographic directions a and b , respectively, and are used to assess the in-plane anisotropy of the exciton (see Supplemental Material [24] for the full definitions of these descriptors).

First, all the bright states are moderately delocalized, Wannier-Mott-like states rather than tightly bound Frenkel excitons. In the bulk the total spread is $R_{\text{exc}} \simeq 10.8$ – 11.2 Å with a 90% containment radius $r_{90} \simeq 14$ Å, and the participation ratio yields an effective $N_{\text{cell}}^{\text{eff}} \simeq 6$ – 7 primitive cells: The correlated pair samples several unit cells, as expected in a screened, extended solid. Upon isolating a single layer the in-plane size does not grow but slightly contracts ($r_{90} \simeq 12.6$ – 13.3 Å), the real-space counterpart of the collapse of dielectric screening that tightens the electron-hole binding in the two-dimensional limit.

Second, the bilayer shows a clear out-of-plane signature. With the hole pinned on a prismatic sulfur of one layer, its in-plane extensions stay bulklike ($R_a, R_b \simeq 5.8$ – 6.6 Å), yet the electron delocalizes across *both* layers, $R_c \simeq 14.7$ Å, inflating R_{exc} and r_{90} to $\simeq 17$ and $\simeq 22$ Å. This is the real-space fingerprint of the interlayer coherence already visible in reciprocal space, where the transverse bilayer exciton couples with nearly equal weight to the two layer-split conduction bands (c_1, c_2): While equal weight need not by itself imply two-layer spread, the real-space extent along c settles it, and the electron shared between c_1 and c_2 in k -space is the same one spread over the two layers in real space.

Third, the optical polarization does *not* map onto the spatial elongation of the pair. The in-plane density is templated

TABLE V. Real-space descriptors of the first bright exciton of each system and polarization, from the Voronoi and participation-ratio analysis of the cube-file excitonic densities (full definitions in the Supplemental Material [24]). E_S is the BSE energy; R_a , R_b , R_c are the root-mean-square electron-hole spreads along the crystallographic axes and $R_{\text{exc}} = (R_a^2 + R_b^2 + R_c^2)^{1/2}$ the total spread; r_{90} is the radius of the smallest hole-centered sphere containing 90% of the excitonic density; $N_{\text{cell}}^{\text{eff}}$ is the effective number of primitive cells sampled by the exciton; S% and Zr% are the fractions of the density residing on the sulfur and zirconium Voronoi basins; Q_a^{xy} and Q_b^{xy} ($Q_a^{\text{xy}} + Q_b^{\text{xy}} = 100\%$) measure the in-plane directional organization of the density. Distances in Å; the chain axis is b in the bulk and a in the 1L/2L slabs, and the out-of-plane R_c is omitted for the isolated monolayer.

System	Pol.	E_S (eV)	R_a	R_b	R_c	R_{exc}	r_{90}	$N_{\text{cell}}^{\text{eff}}$	S%	Zr%	Q_a^{xy}	Q_b^{xy}
Bulk	$\parallel (b)$	2.491	5.99	7.90	5.28	11.22	14.04	5.76	87.82	12.18	27.97	72.03
Bulk	$\perp (a)$	2.409	6.28	6.93	5.40	10.82	14.01	7.43	74.89	25.11	45.05	54.95
1L	$\parallel (a)$	3.028	7.33	5.75		10.46	13.33	10.80	76.44	23.56	66.68	33.32
1L	$\perp (b)$	3.015	6.12	6.49		9.63	12.58	9.90	41.57	58.43	48.28	51.72
2L	$\parallel (a)$	2.746	5.95	5.83	14.71	16.90	21.91	16.37	67.94	32.06	49.24	50.76
2L	$\perp (b)$	2.686	6.36	6.61	14.72	17.34	21.97	13.41	41.88	58.12	46.74	53.26

along the Zr-S chains irrespective of the exciting field: The chain-polarized states are systematically elongated along the chain ($R_{\text{chain}}/R_{\text{transv}} \simeq 1.3$ in the bulk and monolayer, with the in-plane weight biased along the chain, $Q_{\text{chain}}^{\text{xy}} \simeq 72\%$ in the bulk and 67% in the monolayer), whereas the transverse states relax toward in-plane isotropy. Even the transverse bulk exciton keeps a majority of its in-plane weight along the chain ($Q_b^{\text{xy}} \simeq 55\%$). The chain-projected Zr-S network therefore fixes the morphology of the electron-hole correlation, while the polarization acts on the band and $\mathbf{k}$ -space content, a further indication that the chain-parallel and chain-perpendicular states are distinct correlated states.

Finally, the Voronoi decomposition exposes a chemical selection rule tied to the polarization. The chain-longitudinal excitons are chalcogen-centered, carrying 68%–88% of their density on sulfur (S%), whereas the transverse monolayer and bilayer states acquire a majority zirconium character (Zr% $\simeq 58\%$), inherited from the metal-rich lowest conduction bands. The sulfur dominance of the chain-polarized states identifies them as disulfide (S_2)²⁻-derived excitations rather than $\text{S} \rightarrow \text{Zr}$ charge-transfer states.

These results can now be set against the experimental and theoretical literature. Because the available optical data refer to the bulk, we benchmark our bulk excitons against them, the 1L and 2L results being predictions. Table VI collects the relevant near-edge energies, and the agreement is quantitative. The strain-free single-crystal reflectivity of Kurita *et al.* [10] resolves a sharp direct exciton at 2.573 eV for $\mathbf{e} \parallel b$ (chain) and a weaker band at 2.441 eV for $\mathbf{e} \perp b$; the earlier absorption study of Kurita *et al.* [9] places the corresponding A peaks at 2.483 eV ($\parallel$) and 2.450 eV ($\perp$), and the original work of Schairer and Shafer [4] reports the chain-polarized band near 2.53 eV. Our first bright bulk excitons, 2.496 eV ($\parallel b$) and 2.409 eV ($\perp b$), fall close to the measured energies, within ~ 30 –80 meV of the strain-free crystal values and with the correct ordering, the chain-polarized exciton lying above the transverse one, while the computed polarization splitting $E_{\parallel} - E_{\perp} \simeq 0.09$ eV lies inside the experimental window 0.03–0.13 eV. This agreement with three independent experiments is obtained without adjustable parameters. The only previous *ab initio* G_0W_0 -BSE study of bulk ZrS_3 , that of Abdulsalam and Joubert [14], reports lower BSE peaks ($E_A = 2.30$, $E_B = 2.57$ eV) and classifies the lowest state as

resonant, lying above the quasiparticle gap. We attribute this difference to the level of approximation rather than to the physics: Their quasiparticle energies stop at a single, non-self-consistent G_0W_0 correction to PBE, and the calculation uses underconverged parameters. Both choices lower the exciton energies and reduce the binding, so that our better-converged treatment places the bright states slightly higher and as bound excitons, in closer agreement with experiment.

The thinned systems can be confronted with the more recent measurements on exfoliated material, principally the polarized-optics study of Chen *et al.* [45] on ZrS_3 nanoribbons and the photoresponse of few-layer nanoribbons compiled therein. Two points are worth noting. First, on the energies: The ~ 17 nm flakes of Chen *et al.* [45]—the thinnest samples optically characterized to date—still place the near-edge absorption maximum at ~ 2.48 eV, essentially the bulk value, consistent with the weak single-particle layer dependence of the gap noted for the MX_3 family. The blueshift we predict for the true monolayer and bilayer ($E_S \simeq 3.0$ and 2.7 eV) is therefore not visible at 17 nm and is a many-body effect: It is generated by the loss of dielectric screening and the attendant growth of the self-energy in the 2D limit, an ingredient absent from the mean-field gaps and only accessible to a GW-BSE treatment. It constitutes a concrete prediction

TABLE VI. Near-edge optical energies of *bulk* ZrS_3 (eV): present GW-BSE results versus the attached experimental and theoretical literature. E_S denotes the lowest bright BSE state.

Quantity	This work	Literature
Transverse exciton $\mathbf{e} \perp b$	2.41 (E_S)	2.441 ^a , 2.450 ^b
Chain exciton $\mathbf{e} \parallel b$	2.50 (E_S)	2.573 ^a , 2.483 ^b , 2.53 ^c
Splitting $E_{\parallel} - E_{\perp}$	0.09	0.03 ^b –0.13 ^a
BSE peaks A / B	2.41 / 2.50	2.30 / 2.57 ^c
Indirect gap	— ^f	2.02 ^d , 2.06 ^e , 2.06–2.09 ^b
Quasidirect δ	0.10–0.13 ^f	0.11 ^d

^aReference [10].

^bReference [9].

^cReference [4].

^dReference [45].

^eReference [14].

^ffrom the band-structure section.

awaiting monolayer-resolved optical spectroscopy. Second, on the anisotropy: The in-plane dichroism survives and is enhanced toward the few-layer limit, in agreement with our results. Wang *et al.* [46] measure an absorption anisotropy $\alpha_b/\alpha_a = 1.77$ at the 487 nm peak, maximal for $e \parallel b$, and a polarized photocurrent ratio that grows monotonically as the ribbon is thinned—1.53 at 43.2 nm, 1.95 at 15.1 nm, and 2.55 at 3.9 nm—while Chen *et al.* [45] report 1.2–1.7 for their 17 nm flakes, rising to ~ 2 under gating. Our computed first-peak absorption is likewise chain-dominated in the few-layer systems, with dichroic ratios $A_{\parallel}/A_{\perp} \simeq 1.9$ for the bilayer and $\simeq 3.4$ for the monolayer: Both the sign (maximum along the chain b) and the trend (anisotropy increasing as the layer count is reduced) reproduce the nanoribbon data, and the monolayer value lies at, and slightly beyond, the top of the measured progression, exceeding the 2.55 found for the thinnest (3.9 nm) ribbon of Wang *et al.* [46], as expected once the crystal is thinned below any experimentally accessible ribbon. The experimental ratios are extracted from the polarized photocurrent, which additionally folds in the anisotropic carrier mobility, whereas ours is the oscillator-strength ratio of the absorption; that the two agree in sign and magnitude indicates that the polarization selectivity we resolve microscopically is the one measured in the thinned crystals.

The indirect, yet quasidirect, character of the gap that emerges from our assignment is independently confirmed in the literature. The study by Chen *et al.* [45], which combines DFT calculations with polarized-optics measurements, identifies an indirect bulk gap of 2.02 eV (with a Tauc optical gap of about 2.07 eV). The valence-band maximum lies at Γ —a result also observed experimentally by nanoARPES [7]—while the conduction-band minimum falls at Z , only 0.11 eV lower. This small separation corresponds to a quasidirect splitting $\delta = 0.11$ eV, in excellent agreement with the value $\delta \simeq 0.10$ –0.13 eV that we obtain in our own band-structure analysis.

It is precisely this near-degeneracy between Γ and Z that governs the character of the lowest optically active states: They are *zone-edge excitons*—bound electron-hole pairs built from states at the boundary of the Brillouin zone (near Z) rather than at its center (Γ)—lying just above the fundamental edge of the gap. This picture is consistent with the resonant, above-gap bulk exciton described by Abdulsalam and Joubert [14].

The chemistry agrees as well: Following Jellinek and co-workers Jellinek *et al.* [47], both Schairer and Shafer [4] and Kurita *et al.* [10] assign the band edges to disulfide $(S_2)^{2-}$ orbitals (a $\pi_g^* 3p_{xy}$ valence top, a $\sigma_u^* 3p_z$ conduction bottom), so that the dichroism stems from the $(S_2)^{-2}$ wave function anisotropy rather than a metal-centered transition [48]; our real-space densities, which place 75%–88% of the bulk excitonic weight on the sulfur Voronoi basins (Table V), confirm this $(S_2)^{2-}$ -derived, non-charge-transfer character. The polarization dependence merits a final comment, since it is the clearest signature of the anisotropy of ZrS_3 and the literature is itself energy-resolved. Our calculations show that changing the polarization of the exciting field does more than redistribute oscillator strength: It shifts the exciton energy (by ~ 0.09 eV in the bulk and comparably in the slabs) and

changes the nature of the excitation, replacing one set of $v \rightarrow c$ channels by another and moving the dominant e - h amplitude between Γ and the b^* zone edge (Table IV). The chain-parallel and chain-perpendicular excitons are therefore not two polarizations of the same state but two distinct correlated states, which is the microscopic origin of the strong dichroism reported for this material. This is consistent with experiment: Low-temperature strain-free crystals emphasize the sharp direct exciton, strongly chain-polarized ($e \parallel b$ about an order of magnitude stronger than $e \perp b$) [4,10], whereas the polarized-absorption flake data of Chen *et al.* [45] show the near-edge maximum near 2.48 eV to be largest for $e \perp b$, with a wavelength-dependent reversal of the anisotropy axis around 2.25 eV. Our first-peak analysis (Table III) reproduces the low-energy side of this picture: The lowest bright feature of the bulk is the chain-polarized peak at 2.60 eV, sitting just above the transverse $e \perp b$ peak at 2.40 eV—the sharp $e \parallel b$ direct exciton of the strain-free crystals—while the transverse dominance picked up by the flake data is confined to a higher-energy window. Overall, the BSE spectra reproduce the measured exciton energies, polarization splitting, quasidirect δ , and $(S_2)^{2-}$ character of bulk ZrS_3 ; improve on the only earlier G_0W_0 -BSE estimate by going beyond an underconverged G_0W_0 ; and establish, through the real-space descriptors of Table V, that in this quasi-one-dimensional crystal the optical selection rule, the reciprocal-space valley structure, and the sulfur-dominated, chain-templated real-space morphology of the correlated electron density are independent, polarization-selectable observables whose dimensional evolution forms a coherent bulk-to-monolayer picture.

IV. CONCLUSIONS

We have characterized the quasiparticle and excitonic structure of ZrS_3 in its bulk, bilayer, and monolayer forms within parameter-free many-body perturbation theory, combining GW quasiparticle band structures with the solution of the Bethe-Salpeter equation for the polarization-resolved optical response. Our central conclusion is that in this material the electronic and optical excitations cannot be reduced to a renormalized single-particle picture. Self-energy and electron-hole correlation are not small corrections but the ingredients that fix the magnitude, the dimensional behavior, and the polarization identity of the states.

This is clearest in the contrast between the mean-field and the many-body descriptions of the gap. At any fixed level of exact exchange the fundamental gap is nearly independent of thickness—the PBE, HSE06, and PBE0 values vary by less than ~ 0.1 eV between bulk, bilayer, and monolayer—whereas the GW gap opens strongly and monotonically upon thinning, $E_g^{\text{ind}} = 2.46 \rightarrow 3.09 \rightarrow 3.33$ eV for bulk $\rightarrow$ 2L $\rightarrow$ 1L. The self-energy correction over PBE nearly doubles across the same sequence, $\Delta\Sigma = 1.34 \rightarrow 2.02 \rightarrow 2.24$ eV, tracking the progressive collapse of dielectric screening as the third dimension is removed. No single hybrid functional reproduces this trend: The effective global exact-exchange fraction matching the GW gap rises from $\alpha_{\text{eff}} \approx 0.19$ (bulk) to 0.33 (1L), following $\alpha \sim \epsilon_{\infty}^{-1}$, so that the dimensional crossover from a weakly bound bulk semiconductor to a strongly correlated two-dimensional limit is

itself a many-body, environment-dependent effect that no system-independent exchange fraction, and in particular the nontransferable CAM-B3LYP, can capture.

The Bethe-Salpeter spectra place this conclusion on direct experimental footing. In the bulk our lowest bright excitons fall at 2.496 eV ($\mathbf{E} \parallel b$) and 2.409 eV ($\mathbf{E} \perp b$), reproducing the measured absorption edge to within ~ 30 to 80 meV and recovering the correct ordering and the ~ 0.09 eV chain/transverse splitting inside the experimental window (0.03–0.13 eV) reported across half a century of single-crystal work [4,9,10]. This agreement with three independent experiments is obtained without adjustable parameters. The agreement extends to the anisotropy: The computed first-peak dichroic ratios $A_{\parallel}/A_{\perp} \approx 3.4$ (1L) and 1.9 (2L) reproduce both the sign and the thickness trend of the polarization contrast measured on thinned crystals—up to 2.5 in the nanoribbons of Wang *et al.* [46] and 1.2–1.7 in the flakes of Chen *et al.* [45]—with the monolayer value lying at, indeed just beyond, the top of the measured progression, as expected once the crystal is thinned below any experimentally accessible ribbon. A real-space analysis of the excitonic wave functions completes this picture. A compact set of real-space descriptors—the directional second moments $R_{a,b,c}$ and total spread R_{exc} , the 90% containment radius r_{90} , the participation-ratio cell count $N_{\text{cell}}^{\text{eff}}$, the Voronoi sulfur/zirconium weights $S\%/Zr\%$, and the in-plane anisotropy $Q_{a,b}^{\text{xy}}$ —quantify the size, chemical seat, and directional organization of the correlated electron density, and thereby separate a local Frenkel-like exciton from an extended, anisotropic Wannier-Mott-like one. They reveal moderately delocalized excitons ($N_{\text{cell}}^{\text{eff}} \simeq 6$ –16) templated along the Zr-S chains and, in the bilayer, coherently shared between the two layers ($R_c \simeq 14.7$ Å), the real-space counterpart of the interlayer screening resolved in reciprocal space. The chain-polarized bulk states are sulfur-dominated (75%–88% of the density on sulfur), identifying the bright states as $(S_2)^{2-}$ -derived disulfide excitations rather than $S \rightarrow Zr$ charge-transfer states, and confirming the chalcogen-centered band-edge assignment of the early Jellinek-model analyses. Finally, the dimensional and the polarization axes are coupled, and both are governed by correlation. Switching

the light polarization does more than shift the exciton energy: It reorganizes the microscopic identity of the correlated state, sampling distinct valence $\rightarrow$ conduction channels and distinct regions of the Brillouin zone, so that the $\parallel$ and $\perp$ excitons are different physical states rather than two components of one state. The near-edge linear dichroism of the first bright peak is accordingly chain-longitudinal in every system—from the bulk down to the two-dimensional limit—and grows to a maximum in the monolayer. Finally, the predicted blueshift of the optical onset (bulk ~ 2.4 eV $<$ 2L ~ 2.8 eV $<$ 1L ~ 3.0 eV) is not yet visible in the ~ 17 nm flakes measured to date [45], whose response remains pinned at the bulk value; it is a genuine many-body prediction, rooted in the screening collapse of the truly two-dimensional limit, and constitutes a concrete target for polarization-resolved spectroscopy on isolated monolayer ZrS_3 . The discrepancy with the single-shot G_0W_0 estimate of Abdulsalam and Joubert [14] is traced not to a conceptual disagreement but to their stopping at one non-self-consistent iteration with underconverged GW parameters. Taken together, these results establish ZrS_3 as a system whose excitonic physics is governed by many-body effects at every level—magnitude, dimensionality, and polarization—and provide a quantitative, experimentally validated benchmark for the quasi-one-dimensional trichalcogenide family.

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DATA AVAILABILITY

There are no publicly available research data or software supporting this manuscript. Requests for further information or data should be sent to the authors.

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