

Article

Effect of a Stoichiometric Trefoil-like Rotational Reconstruction on the Electronic and Optical Properties of WS₂ and WSe₂ Monolayers

Daulet Sergeyev ^{1,2,*} , Gulbanu Serikbayeva ¹ and Ainur Duisenova ¹¹ Department of Physics, K. Zhubanov Aktobe Regional University, Aktobe 030000, Kazakhstan² Department of General Engineering Disciplines, T. Begeldinov Aktobe Aviation Institute, Aktobe 030012, Kazakhstan

* Correspondence: serdau82@gmail.com; Tel.: +7-708-188-90-24

Abstract

Structural defects provide an effective means of tailoring the electronic and optical properties of two-dimensional transition-metal dichalcogenides. In this work, the structural, electronic, and polarization-resolved optical properties of pristine WS₂ and WSe₂ monolayers and their stoichiometric trefoil-like rotational reconstructions were investigated using density functional theory. The reconstruction was generated through a local 60° bond rotation without removing or adding atoms and therefore differs fundamentally from the experimentally observed chalcogen-deficient T₁(3DV) defect. Electronic-structure calculations were performed using the PBE-GGA + U and SOGGA approaches, with noncollinear spin–orbit coupling included in the latter, while the optical response was evaluated within the independent-particle Kubo–Greenwood formalism. Structural relaxation revealed two distinct regimes. In WS₂, the reconstruction produced a largely compensated redistribution of W–S bond lengths, with the mean distance remaining nearly unchanged, whereas WSe₂ exhibited a net expansion of the W–Se coordination network and substantially stronger out-of-plane buckling. The reconstruction introduced additional W 5*d*–chalcogen *p* states near the band edges and markedly reduced the electronic band gaps. For WS₂, the gap decreased from 1.87 to 1.55 eV within DFT + U and from 1.96 to 1.46 eV within SOGGA. A substantially stronger response was obtained for WSe₂, for which the corresponding gaps decreased from 1.533 to 0.751 eV and from 1.657 to 0.645 eV. The reconstructed monolayers exhibited pronounced optical anisotropy, red-shifted absorption edges, spectral broadening, and additional low-energy in-plane optical transitions. These effects were particularly strong in WSe₂, where the calculated optical response extended into the near-infrared region. The results demonstrate that the electronic and optical response to a stoichiometric trefoil-like reconstruction is strongly chalcogen-dependent and is governed by the interplay among local geometrical distortion, W 5*d*–chalcogen *p* hybridization, and spin–orbit coupling.

Keywords: transition metal dichalcogenides; WS₂ monolayer; WSe₂ monolayer; trefoil-like rotational reconstruction; topological defects; density functional theory; electronic structure; optical absorption; defect engineering



Academic Editors: Grazia
Giuseppina Politano and
John Parthenios

Received: 14 August 2026

Revised: 30 August 2026

Accepted: 2 September 2026

Published: 6 September 2026

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1. Introduction

Group-VI transition-metal dichalcogenides (TMDs) have emerged as one of the most promising classes of two-dimensional semiconductors owing to their unique combination of layer-dependent electronic structure, strong spin–orbit coupling, reduced dielectric

screening, and pronounced light-matter interaction [1–5]. Rapid progress in this field began with the successful isolation and identification of atomically thin two-dimensional crystals. One of the most significant breakthroughs was the experimental demonstration of the transition of MoS₂ from an indirect-band-gap semiconductor in the bulk phase to a direct-band-gap semiconductor in the monolayer limit, accompanied by a dramatic enhancement of photoluminescence [6,7]. The subsequent realization of field-effect transistors based on monolayer MoS₂ further confirmed the potential of TMDs for atomically thin electronic devices [8,9]. The discovery of valley-selective optical excitation using circularly polarized light, together with the possibility of optically manipulating valley polarization, established the physical foundation of TMD-based valleytronics [10–12].

Subsequent studies revealed pronounced excitonic effects in TMDs and demonstrated that their electronic band structure and optical response can be effectively tailored through mechanical strain, dielectric environment, and interlayer coupling [13–15]. The development of vertical, lateral, and moiré van der Waals heterostructures has greatly expanded the functional capabilities of these materials for applications in field-effect transistors, photodetectors, light-emitting devices, tunnel diodes, and other nanoelectronic and optoelectronic components. Current research is focused on the controlled synthesis of such heterostructures, manipulation of interlayer excitons, spin–valley states, and moiré electronic phases, as well as the integration of TMDs with dielectric and electrode layers, while minimizing damage to the atomically thin semiconductor [16–18].

In our previous studies, we investigated various approaches for tuning the electronic, optical, and transport properties of low-dimensional TMD systems, including the application of external electric fields, modification of nanostructure geometry, interlayer hybridization, and the formation of van der Waals and moiré heterointerfaces. Our results obtained for two-dimensional TMD/Janus heterostructures, monolayer and coaxial TMD nanotubes, and model nanodiodes demonstrated that these approaches enable substantial modulation of the electronic band structure, optical response, and charge transport characteristics [19–24]. These findings indicate that the functional properties of TMD-based systems are governed not only by their chemical composition but also by their dimensionality, structural geometry, relative orientation of constituent layers, interlayer hybridization, and local atomic configuration.

Particular attention has been devoted to monolayer WS₂ and WSe₂, which are among the most representative members of the TMD family. In the monolayer limit, both materials exhibit direct optical transitions at the K/K' valleys of the Brillouin zone. The absence of inversion symmetry, together with the large spin–orbit splitting of the valence bands originating predominantly from W *d* orbitals, gives rise to strong spin–valley coupling [25–27]. These unique characteristics make WS₂ and WSe₂ highly attractive for applications in photodetectors, light-emitting devices, valleytronic components, and ultrathin photovoltaic systems. However, their optical properties cannot be adequately described within the framework of a simple independent-particle approximation. Reduced dielectric screening and two-dimensional quantum confinement lead to the formation of strongly bound excitons, causing the experimentally observed A- and B-excitonic resonances to appear substantially below the quasiparticle band gap [28–30].

The properties of real TMD monolayers are governed not only by their ideal crystal lattice but also by structural defects introduced during crystal growth, transfer, thermal processing, and electron-beam irradiation [31]. Chalcogen and metal vacancies, antisite defects, substitutional impurities, grain boundaries, and reconstructed vacancy complexes may introduce localized electronic states, modify the carrier concentration and mobility, activate nonradiative recombination channels, and give rise to bound-exciton emission [31–35]. Combined experimental investigations using atomic-resolution microscopy and first-

principles calculations have demonstrated that both the type and concentration of these defects strongly depend on the synthesis conditions and subsequent post-growth treatment. Consequently, defect engineering plays a dual role: while uncontrolled defects may degrade the electronic transport and luminescence properties of TMD monolayers, their deliberate introduction or passivation provides an effective route for tailoring the doping level, optical emission, and catalytic activity of these materials.

A distinct class of topological defects originates from local bond rotations. The best-known example is the Stone–Wales defect in sp^2 -bonded carbon materials [36–38]. In graphene, this defect is generated by a 90° rotation of a single C–C bond without the addition or removal of atoms. As a result, four adjacent hexagonal rings are transformed into two pentagons and two heptagons, producing the characteristic 5-7-7-5 ring configuration. Although this topological transformation preserves the stoichiometry of the lattice, it modifies the local symmetry, strain distribution, and electronic structure. In our previous studies, the influence of Stone–Wales defects on the electronic transport properties of graphene clusters and single-walled carbon nanotubes was systematically investigated [39,40]. The obtained results demonstrated that such local topological reconstructions generate characteristic defect-induced electronic states and can significantly modify the current-voltage characteristics and differential conductance of carbon nanostructures.

The trigonal–prismatic heteroatomic MX_2 lattice does not permit a direct single-bond analog of the Stone–Wales transformation without generating energetically unfavorable homoatomic bonds. Lin et al. demonstrated that a concerted 60° rotation of three neighboring metal–chalcogen bond pairs can produce a threefold-symmetric rotational reconstruction referred to as a trefoil defect [41]. Using in situ scanning transmission electron microscopy (STEM), these defects were experimentally observed in WSe_2 , WS_2 , and $MoSe_2$, where their formation and migration were associated with electron-beam-induced chalcogen vacancies. The simplest experimentally identified first-order defect, denoted T_1 , consists of three octagonal rings and is most consistently described by the metal-centered, chalcogen-deficient $T_1(3DV)$ model containing three chalcogen divacancies. Successive concerted bond rotations may further increase the defect size, giving rise to higher-order rotational reconstructions and ultimately leading to the formation of extended 8-5-5-8 grain boundaries.

The structural model considered in the present work differs fundamentally from the experimentally identified vacancy-containing $T_1(3DV)$ defect. The rotational reconstruction investigated here is generated within the supercell without the addition or removal of atoms and therefore preserves the stoichiometric composition of the WS_2 and WSe_2 monolayers. In this respect, it is conceptually analogous to the Stone–Wales defect in graphene, since in both cases the local topological reconstruction is produced solely through bond rotation while maintaining the total number of atoms. Accordingly, the structure considered here is referred to as a stoichiometric trefoil-like rotational reconstruction rather than the experimentally observed $T_1(3DV)$ vacancy defect. This distinction is essential because the geometric similarity between the two reconstructions does not imply identical formation mechanisms, formation energies, or thermodynamic stability.

First-principles calculations by Lin et al. demonstrated that rotational defects in WSe_2 can give rise to defect-induced in-gap states localized at the corners of the defect, electronic states near the band edges associated with reconstructed boundaries, p -type conductivity in larger defect complexes, and localized magnetic moments, while only weakly affecting the overall mechanical response of the material [41]. These findings indicate that trefoil-like reconstructions are electronically active topological defects rather than merely geometrical distortions of the crystal lattice. However, their influence on the polarization-resolved optical response of technologically important WS_2 and WSe_2 monolayers has received considerably less attention than that of conventional vacancy defects. In particular, a

systematic comparative investigation is required to clarify how replacing S with the larger and more polarizable Se atom influences local structural relaxation, hybridization between $W-d$ and chalcogen- p states, band-gap modification, and the emergence of low-energy optical transitions.

A quantitative description of defect-induced electronic states in two-dimensional materials remains a challenging theoretical problem. Semilocal density-functional approximations generally underestimate the quasiparticle band gap. Moreover, localized defect states and extended band states experience different degrees of dielectric screening, implying that a single empirical correction does not necessarily provide a consistent description of both types of electronic states [42]. For W-based TMDs, an accurate treatment of spin–orbit coupling is also essential. Furthermore, optical spectra calculated within the independent-particle linear-response approximation neglect electron–hole interactions and therefore should not be directly compared with experimentally observed excitonic resonances. Nevertheless, comparing results obtained using different exchange–correlation functionals provides a useful means of assessing the robustness of the predicted physical trends, provided that the method-dependent absolute energy values are interpreted with appropriate caution.

In this work, we investigate pristine WS_2 and WSe_2 monolayers together with their stoichiometric trefoil-like rotational reconstructions by means of density functional theory calculations employing the DFT + U and SOGGA approaches, with spin–orbit coupling explicitly included in the latter. In contrast to the previously reported chalcogen-deficient $T_1(3DV)$ model, the reconstruction considered here is generated without removing or adding atoms and therefore preserves the stoichiometric composition of the monolayer. We systematically analyze the distributions of bond lengths and bond angles following structural relaxation, out-of-plane lattice distortion, total and orbital-projected electronic densities of states, band-gap modification, and the polarization-resolved optical response. The primary objective of this work is to establish the general trends governing the influence of the stoichiometric trefoil-like rotational reconstruction on the electronic and optical properties of WS_2 and WSe_2 and to elucidate the physical origin of the more pronounced sensitivity of WSe_2 to local bond rotation. The use of the same reconstruction model for both monolayers provides a direct basis for identifying the role of the chalcogen species in determining the structural, electronic, and optical response. Our results demonstrate that the reconstruction introduces hybridized $W-5d$ /chalcogen- p states near the band edges, reduces the band gap, and gives rise to additional low-energy optical transitions, with the most significant structural and electronic modifications occurring in WSe_2 .

2. Methods

The electronic structure and optical properties of pristine and trefoil-defective WS_2 and WSe_2 monolayers were investigated within the framework of density functional theory (DFT) as implemented in the Atomistix ToolKit Virtual NanoLab 2015.1 (ATK-VNL) [43]. To evaluate the influence of the exchange–correlation functional on the calculated electronic and optical properties, two computational approaches were employed. The first approach utilized the Perdew–Burke–Ernzerhof generalized gradient approximation with an on-site Hubbard correction (PBE-GGA + U) [44,45]. An effective on-site Hubbard parameter of $U = 3.0$ eV was applied to the W $5d$ orbitals to improve the description of localized electron states. The second approach was based on the second-order generalized gradient approximation (SOGGA) combined with noncollinear spin–orbit coupling (SOC), allowing an explicit treatment of relativistic effects that are particularly important for tungsten-based transition metal dichalcogenides.

For both computational approaches, the electronic wave functions were expanded using a double-zeta polarized (DZP) numerical atomic orbital basis set together with FHI norm-conserving pseudopotentials. Self-consistent field (SCF) calculations were performed using the Pulay mixing algorithm with a convergence tolerance of 1×10^{-6} Hartree, a maximum of 200 SCF iterations, and a density mesh cutoff of 125 Hartree. The electronic temperature was set to 100 K using Fermi-Dirac smearing. The PBE-GGA + U calculations were carried out within the non-spin-polarized approximation, whereas the SOGGA calculations included noncollinear spin-orbit coupling.

The Brillouin zone was sampled using a $15 \times 15 \times 1$ Monkhorst-Pack k-point mesh. Periodic boundary conditions were applied in the in-plane directions, while Neumann boundary conditions were imposed along the direction perpendicular to the monolayer. The electrostatic potential was calculated using the multigrid Poisson solver. All calculations were performed for charge-neutral systems.

After complete structural optimization, the optical properties were calculated within the framework of linear response theory using the Kubo-Greenwood formalism. The frequency-dependent complex dielectric function was obtained from the dipole transition matrix elements between occupied and unoccupied electronic states according to the Kubo-Greenwood equation [46,47]:

$$\chi_{ij}(\omega) = \frac{e^2}{\hbar m_e^2 V} \sum_{nm\mathbf{k}} \frac{f_{m\mathbf{k}} - f_{n\mathbf{k}}}{\omega_{nm}^2(\mathbf{k})[\omega_{nm}(\mathbf{k}) - \omega - i\Gamma/\hbar]} p_{nm}^i(\mathbf{k}) p_{mn}^j(\mathbf{k}), \quad (1)$$

where $p_{nm}^i(\mathbf{k}) = \langle n\mathbf{k} | \hat{p}_i | m\mathbf{k} \rangle$ is the i -th Cartesian component of the momentum matrix element between electronic states n and m , V is the supercell volume, Γ is the energy-broadening parameter, $f_{n\mathbf{k}}$ is the Fermi-Dirac occupation factor, and $\hbar\omega_{nm}(\mathbf{k}) = E_{n\mathbf{k}} - E_{m\mathbf{k}}$.

The complex dielectric function describing the optical response of the investigated monolayers is expressed as

$$\varepsilon(\omega) = 1 + \chi(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega), \quad (2)$$

where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ denote the real and imaginary parts of the dielectric function, respectively. The real part characterizes the dispersive properties of the material and determines the phase variation in the transmitted electromagnetic radiation, whereas the imaginary part is directly related to interband optical absorption and describes energy dissipation within the system.

The refractive index $n(\omega)$ and the extinction coefficient $k(\omega)$ were obtained from the calculated dielectric function using the Kramers-Kronig relations:

$$k(\omega) = \sqrt{\frac{\sqrt{\text{Re}(\varepsilon)^2 + \text{Im}(\varepsilon)^2} - \text{Re}(\varepsilon)}{2}} \quad (3)$$

$$n(\omega) = \sqrt{\frac{\sqrt{\text{Re}(\varepsilon)^2 + \text{Im}(\varepsilon)^2} + \text{Re}(\varepsilon)}{2}} \quad (4)$$

The optical absorption coefficient, $\alpha(\omega)$, which characterizes the attenuation of electromagnetic radiation propagating through the investigated monolayers, was subsequently calculated as

$$\alpha = 2\frac{\omega}{c}k. \quad (5)$$

The calculated dielectric function, refractive index, extinction coefficient, and absorption coefficient provide comprehensive information on the optical response of pristine and

trefoil-defective WS₂ and WSe₂ monolayers. Analysis of these spectra enables identification of the dominant interband electronic transitions, evaluation of defect-induced modifications of the optical properties, and determination of the photon-energy regions exhibiting enhanced light absorption.

Structural optimization was performed using the LBFGS algorithm until the maximum residual atomic force was below 0.02 eV Å^{−1}. During the optimization, the lattice parameters were kept fixed and only the atomic coordinates were relaxed. The density of states was evaluated using a denser 30 × 30 × 1 Monkhorst-Pack grid. The polarization-resolved optical properties were calculated within the Kubo-Greenwood formalism using a 45 × 45 × 1 Monkhorst-Pack k-point grid. A broadening parameter of $\Gamma = 0.05$ eV was employed to provide sufficient smoothing of the discrete interband transitions while preserving the principal spectral features. The same broadening parameter was applied consistently to all pristine and reconstructed structures to ensure a direct comparison of their optical responses. The optical spectra were evaluated over the photon-energy range of 0–5 eV using 501 energy points.

All calculations were carried out on a Supermicro high-performance computing server equipped with an Intel® Xeon® Silver processor (Super Micro Computer, Inc., San Jose, CA, USA, distributor PolyWorks Company), 512 GB RAM, and 64 CPU cores. Electronic structure and optical property calculations were performed using the Atomistix ToolKit Virtual NanoLab (ATK-VNL) software package [43]. The theoretical foundations of the DFT methodology and the numerical implementation employed in this work are described in detail elsewhere [48–50].

3. Structural Geometry and Local Reconstruction

The atomic structures of pristine and trefoil-defective WS₂ and WSe₂ monolayers are shown in Figure 1. Both systems were modeled using 5 × 5 × 1 hexagonal supercells containing 25 W atoms and 50 chalcogen atoms. The in-plane supercell parameter is 15.766 Å for WS₂ and 16.410 Å for pristine WSe₂, while a vacuum spacing larger than 30 Å was introduced along the out-of-plane direction to suppress interactions between periodically repeated monolayers. This vacuum separation was chosen to minimize spurious interactions between periodically repeated images of the monolayer along the out-of-plane direction. The corresponding primitive-cell lattice constants are approximately 3.153 Å for WS₂ and 3.282 Å for WSe₂.

The pristine monolayers preserve the characteristic trigonal-prismatic coordination of the 2H phase, in which the tungsten sublattice is located in the central plane and the chalcogen atoms form two symmetric sublayers above and below it. In the ideal WS₂ structure, all six nearest-neighbor W-S bonds are equivalent and have a length of 2.405 Å. The corresponding W-Se bond length in pristine WSe₂ is 2.526 Å. The absence of a measurable bond-length dispersion in the pristine supercells confirms their translational and local coordination symmetry.

The trefoil defect was introduced through a local 60° rotation of a triangular structural fragment, followed by reconstruction of the surrounding coordination network. The resulting configuration preserves the total number of atoms and the chemical composition of the monolayer; therefore, it represents a topological bond rearrangement rather than a vacancy-type defect. The reconstruction forms a characteristic three-lobed defect core and strongly breaks the local rotational and translational symmetry.

A quantitative analysis of the nearest-neighbor distances shows that the defect produces a substantial redistribution of W-X bond lengths. In defective WS₂, the W-S distances vary from 2.298 to 2.488 Å, compared with the uniform pristine value of 2.405 Å. These limiting values correspond to a maximum bond contraction of approximately 4.42% and a

maximum elongation of 3.45%. However, the average W-S bond length remains nearly unchanged, increasing only from 2.405 to 2.406 Å. This result indicates that the defect-induced strain in WS₂ is predominantly local and compensated: shortened and elongated bonds coexist within the reconstructed region without producing a significant net expansion of the lattice.

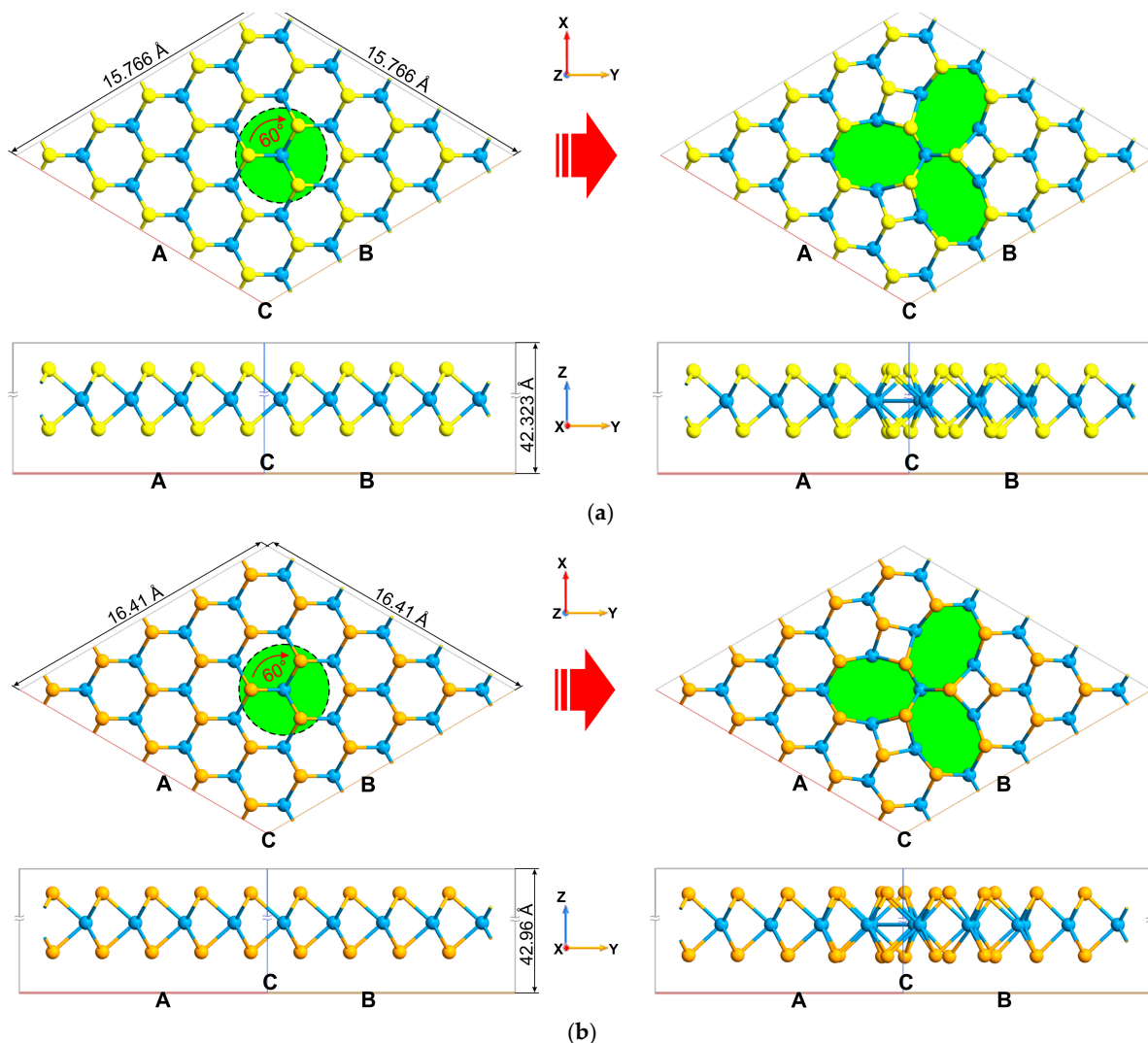


Figure 1. Formation mechanism and atomic structures of the trefoil defect in monolayer transition metal dichalcogenides: (a) WS₂ and (b) WSe₂. For each material, the left panels show the pristine monolayer and the right panels show the trefoil-defective monolayer. The defect is formed by a local 60° rotation of the highlighted atomic region. Top and side views are presented.

A more pronounced reconstruction is observed in WSe₂. The W-Se bond lengths in the defective structure range from 2.464 to 2.696 Å, whereas the pristine value is 2.526 Å. The maximum bond contraction is approximately 2.45%, while the maximum elongation reaches 6.71%. In contrast to WS₂, the average W-Se bond length increases noticeably to 2.594 Å. The corresponding standard deviations of the W-X bond-length distributions are 0.038 Å for defective WS₂ and 0.046 Å for defective WSe₂, demonstrating a broader and more asymmetric local strain distribution in the selenium-based monolayer (Table 1). Here, the bond-length standard deviation (SD) characterizes the dispersion of the W-X bond lengths around their mean value and serves as a simple quantitative measure of local structural distortion.

Table 1. Structural parameters of pristine and trefoil-defective WS₂ and WSe₂ monolayers.

Structure	Mean W–X Bond, Å	Min W–X, Å	Max W–X, Å	Bond-Length SD, Å	Mean Thickness, Å	Maximum Thickness, Å
Pristine WS ₂	2.405	2.405	2.405	0.000	3.142	3.142
Defective WS ₂	2.406	2.298	2.488	0.038	3.174	3.233
Pristine WSe ₂	2.526	2.526	2.526	0.000	3.341	3.341
Defective WSe ₂	2.594	2.464	2.696	0.046	3.558	3.660

The trefoil reconstruction also strongly modifies the local bond angles. For the pristine structures, the characteristic same-sublayer X–W–X angles are 81.93° for WS₂ and 81.03° for WSe₂. In defective WS₂, these angles spread over a wide interval from 59.41° to 96.50°, with an average value of 80.52°. In defective WSe₂, the corresponding interval is 59.08–91.80°, and the average angle decreases to 77.51°. A similar broadening is observed for the W–X–W angles, which vary from 67.38° to 86.26° in defective WS₂ and from 63.89° to 83.64° in defective WSe₂. These large angular deviations confirm that the trefoil defect affects not only individual bond lengths but also the complete local coordination geometry.

In the present analysis, the monolayer thickness is defined by the vertical separation between the upper and lower chalcogen sublayers, while the maximum thickness reflects the largest local separation within the reconstructed region.

The side views reveal an additional out-of-plane relaxation of the chalcogen sublayers. The pristine monolayer thickness, defined as the vertical separation between the upper and lower chalcogen planes, is 3.142 Å for WS₂ and 3.341 Å for WSe₂. In defective WS₂, the average thickness increases to 3.174 Å, while the maximum local thickness reaches 3.233 Å. For WSe₂, the average thickness increases more substantially to 3.558 Å, with a maximum local value of 3.660 Å. Thus, the maximum thickness enhancement is approximately 2.9% in WS₂ and 9.5% in WSe₂. The tungsten sublattice remains essentially planar, whereas the main vertical relaxation is accommodated by the sulfur and selenium atoms.

These results demonstrate two distinct structural-relaxation regimes. In WS₂, the defect mainly produces a compensated redistribution of compressed and elongated bonds around an almost unchanged mean W–S distance. In WSe₂, the reconstruction involves both bond-length dispersion and an overall local expansion of the W–Se network, accompanied by substantially stronger out-of-plane buckling. This difference indicates that the WSe₂ monolayer is structurally more compliant in the vicinity of the trefoil defect.

The observed bond-length redistribution, angular distortion, and local buckling break the equivalence of the tungsten coordination sites and modify the overlap between W 5*d* orbitals and chalcogen *p* orbitals. Consequently, the trefoil defect is expected to alter the band-edge states, introduce defect-related features in the density of states, and modify the polarization-dependent optical response. The structural analysis therefore provides the microscopic basis for the electronic and optical changes discussed in the following sections.

To complement the structural analysis and assess the energetic feasibility and local stability of the proposed trefoil-like reconstruction, additional total-energy and structural-relaxation calculations were performed.

To further assess the energetic feasibility of the proposed stoichiometric trefoil-like reconstruction, additional total-energy calculations were performed for WS₂ and WSe₂ monolayers. Since the pristine and reconstructed structures have identical stoichiometry, the energetic cost of the reconstruction was evaluated directly from the total-energy difference, $E_{\text{rec}} = E_{\text{trefoil}} - E_{\text{pristine}}$, without introducing atomic chemical potentials. The reconstructed WS₂ configuration lies approximately 14.19 eV above the pristine structure,

indicating that the trefoil reconstruction represents a high-energy metastable configuration rather than the thermodynamic ground state.

In addition, a sequence of intermediate configurations connecting the pristine and trefoil-like structures was constructed to examine the evolution of the total energy along the structural transformation pathway. As shown in Figure 2a, the relative energy of WS₂ increases progressively from the pristine configuration and reaches a maximum of approximately 19.05 eV at intermediate image #6, followed by a decrease toward the trefoil-like configuration at approximately 14.19 eV. Thus, the maximum along the considered interpolated pathway lies approximately 4.86 eV above the final reconstructed state. It should be emphasized that this profile is based on the total energies of intermediate configurations and is therefore used here as an energetic characterization of a plausible structural transformation pathway rather than as a rigorously optimized NEB activation barrier.

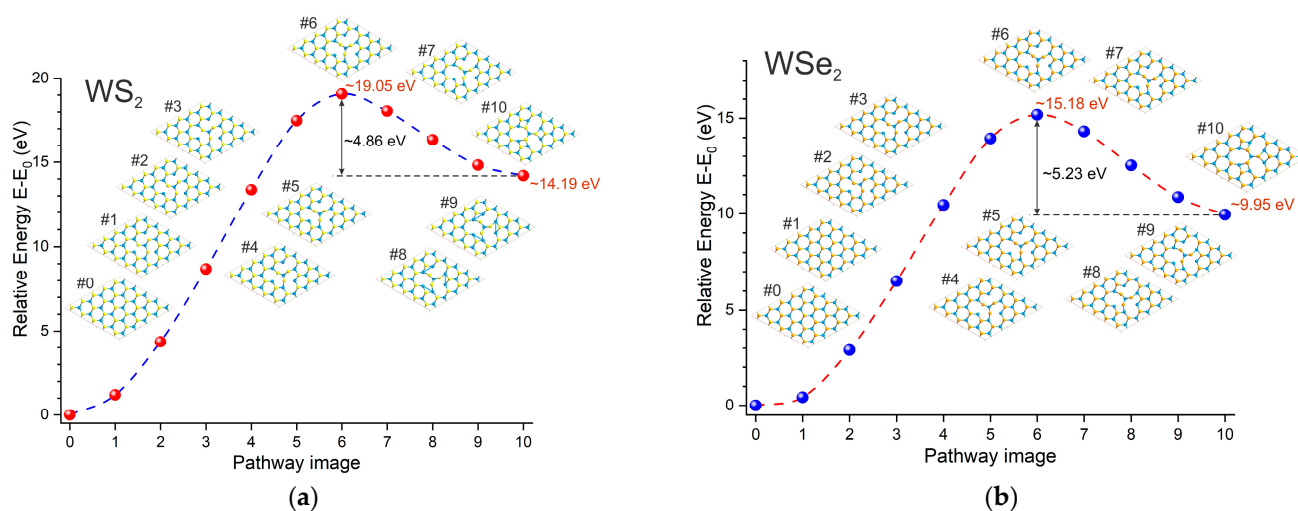


Figure 2. Relative total-energy profiles along the interpolated structural transformation pathway from pristine to stoichiometric trefoil-like reconstructed monolayers: (a) WS₂ and (b) WSe₂. The energies are referenced to the corresponding pristine structures (E_0). Selected intermediate atomic configurations illustrate the progressive bond rearrangement leading to the trefoil-like topology. The maximum energies along the considered pathways are approximately 19.05 eV for WS₂ and 15.18 eV for WSe₂. The final reconstructed configurations remain approximately 14.19 and 9.95 eV above the corresponding pristine structures, respectively.

A qualitatively similar energy profile is obtained for WSe₂ (Figure 2b). The energy initially increases with progressive bond rearrangement, reaches a maximum of approximately 15.18 eV at image #6, and subsequently decreases toward the final trefoil-like configuration. The reconstructed state remains approximately 9.95 eV above the pristine structure, while the maximum along the considered pathway is approximately 5.23 eV above the final reconstructed state. The lower energetic cost and lower maximum energy encountered along the considered pathway for WSe₂ compared with WS₂ suggest that the trefoil-like bond reconstruction is energetically more accessible in WSe₂ within the present computational model.

These results do not imply spontaneous formation of the trefoil reconstruction under equilibrium conditions. Rather, its relatively high energy with respect to the pristine monolayer indicates that an external energy input would be required to produce the associated bond rearrangement. Such conditions may potentially occur under strongly nonequilibrium excitation, for example during energetic particle or electron irradiation, local thermal excitation, or intense pulsed energy deposition. Once formed, the reconstructed configuration may persist as a metastable state if its return to the pristine lattice is

kinetically hindered. Therefore, the present calculations establish the energetic plausibility of the proposed bond-rotation reconstruction but do not constitute direct evidence of its experimental realization.

As an additional test of the local structural stability of the proposed reconstruction, the trefoil-like WS₂ and WSe₂ configurations were subjected to independent atomistic relaxation using the USPEX workflow with the MatterSim/ASE relaxation engine [51–53]. Importantly, the characteristic bonding topology was preserved in both systems after relaxation. For WS₂, all 150 W-S bonds identified in the initial reconstructed configuration were retained, with no bond breaking or formation of new W-S connections. The same behavior was observed for WSe₂, for which all 150 W-Se bonds were preserved. After accounting for the accompanying lattice relaxation, the mean atomic displacements were approximately 0.023 Å for WS₂ and 0.092 Å for WSe₂, with maximum displacements of approximately 0.073 and 0.190 Å, respectively. These results indicate that the trefoil-like configurations do not spontaneously collapse back to the pristine hexagonal topology during structural relaxation and provide additional evidence that the proposed reconstructions can represent locally stable configurations on the potential-energy landscape.

4. Results and Discussion

Figures 3 and 4 presents the projected density of states (PDOS) of pristine and trefoil-defective WS₂ monolayers. In the pristine structure, the valence band maximum is primarily formed by hybridized S-3*p* and W-5*d* states, whereas the conduction band minimum is dominated by W-5*d* orbitals. Deep valence states located near −13 eV originate mainly from S-3*s* orbitals and remain almost unchanged.

The introduction of the trefoil defect leads to a pronounced redistribution of the electronic density of states. Numerous additional sharp peaks appear within both the valence and conduction bands, indicating the formation of localized defect-related electronic states due to local symmetry breaking. The most significant modifications occur in the W 5*d* and S 3*p* states, indicating a pronounced defect-induced redistribution and modification of the *d*-*p* orbital mixing near the band edges.

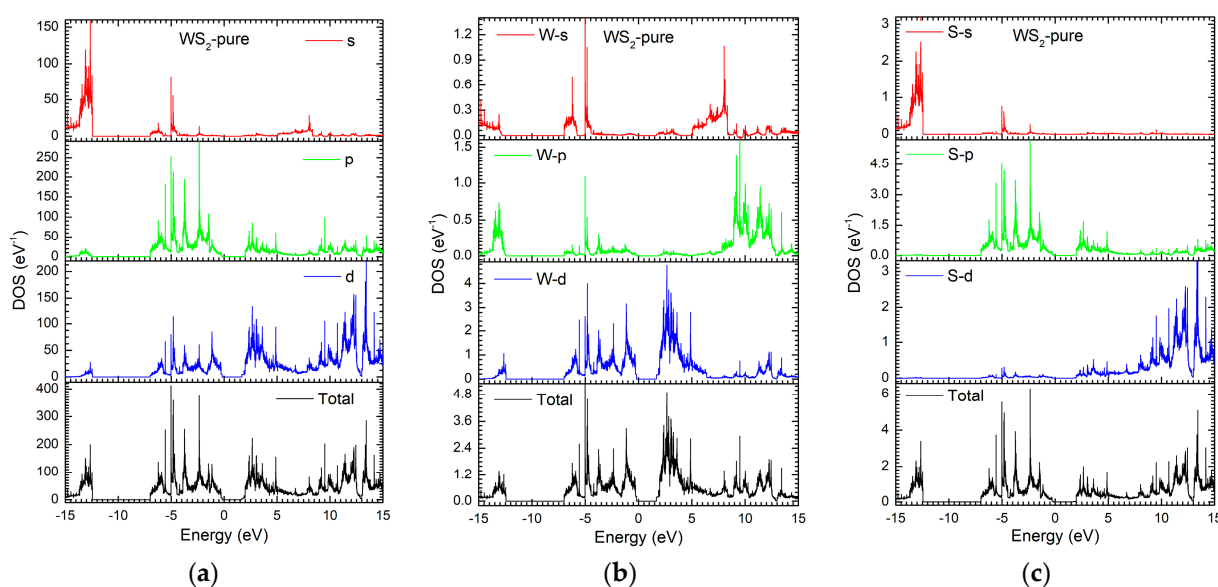


Figure 3. Total and orbital-projected density of states (DOS and PDOS) of pristine WS₂: (a) total orbital-resolved DOS, showing the *s*-, *p*-, and *d*-state contributions; (b) W-projected DOS, showing the W-*s*-, W-*p*-, and W-*d* contributions; (c) S-projected DOS, showing the S-*s*-, S-*p*-, and S-*d* contributions.

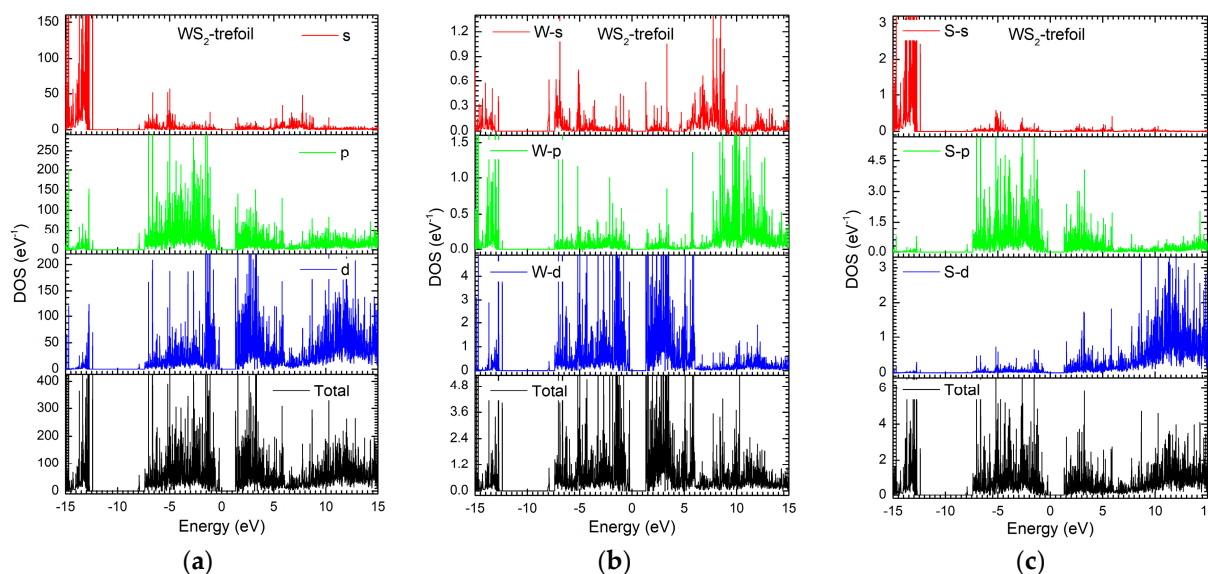


Figure 4. Total and orbital-projected density of states (DOS and PDOS) of trefoil-defective WS₂: (a) total orbital-resolved DOS, showing the *s*, *p*, and *d* state contributions; (b) W-projected DOS, showing the W-*s*, W-*p*, and W-*d* orbital contributions; (c) S-projected DOS, showing the S-*s*, S-*p*, and S-*d* orbital contributions.

These orbital rearrangements are directly reflected in the electronic band gap. (The reported band-gap values were determined from the energy interval with vanishing electronic density of states around the Fermi level.) According to the DOS analysis, the band gap decreases from 1.87 to 1.55 eV within the DFT + U approach and from 1.96 to 1.46 eV using the SOGGA functional. Thus, the trefoil defect reduces the band gap by 0.32 eV (17%) and 0.50 eV (26%), respectively. The reduction originates from the appearance of defect-induced localized W-5*d*/S-3*p* states near the band edges, which effectively narrow the energy separation between the valence and conduction bands.

The calculated optical transitions may be associated with the experimentally observed excitonic resonances (A and B excitons) reported for monolayer TMD [54]. However, the present DFT calculations do not explicitly include electron-hole interactions; therefore, the obtained peaks should be interpreted primarily as interband optical transitions, while excitonic effects are expected to modify their energies and intensities.

To clarify the influence of the trefoil defect on the electronic structure of the WSe₂ monolayer, the total and projected density of states (DOS and PDOS) were analyzed for both pristine and defective systems (Figures 5 and 6).

The total DOS of the pristine WSe₂ monolayer exhibits a well-defined forbidden energy region around the Fermi level, confirming its semiconducting nature. According to the DOS calculations, the band gap amounts to 1.533 eV within the DFT + U approach and 1.657 eV using the SOGGA functional (Table 2). (Accordingly, DFT + U and SOGGA are not used here to define upper and lower bounds of the predicted band gaps. Instead, their comparison serves as a cross-method consistency check to assess the robustness of the defect-induced electronic-structure trends with respect to the exchange-correlation treatment. Although the absolute band-gap values differ between the two approaches, both consistently predict a substantial gap reduction upon trefoil reconstruction and a considerably stronger relative response for WSe₂ than for WS₂.) The valence-band maximum (VBM) is mainly composed of hybridized W 5*d* and Se 4*p* states, whereas the conduction-band minimum (CBM) is dominated by W 5*d* orbitals with a smaller contribution from Se 4*p* states. Such orbital distribution agrees well with the electronic structure generally reported for transition-metal

dichalcogenides, where the transition-metal d orbitals primarily determine the electronic properties near the Fermi level.

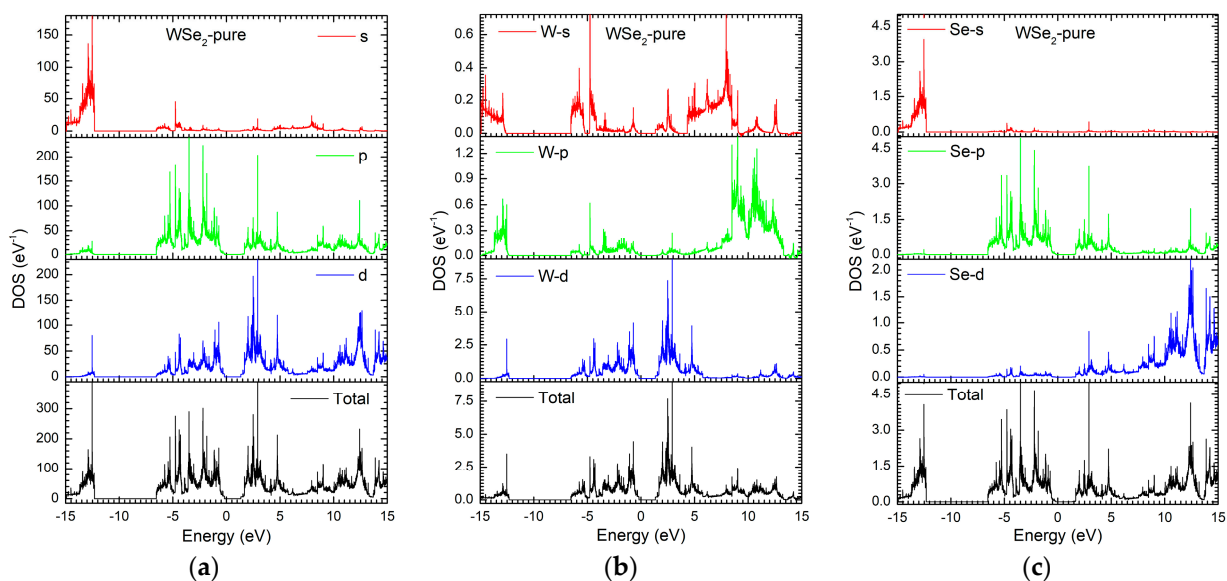


Figure 5. Total and orbital-projected density of states (DOS and PDOS) of pristine WSe₂: (a) Total orbital-resolved density of states, showing the s -, p -, and d -state contributions together with the total DOS; (b) W-projected density of states (PDOS), showing the contributions of W- s , W- p , and W- d orbitals; (c) Se-projected density of states (PDOS), showing the contributions of Se- s , Se- p , and Se- d orbitals.

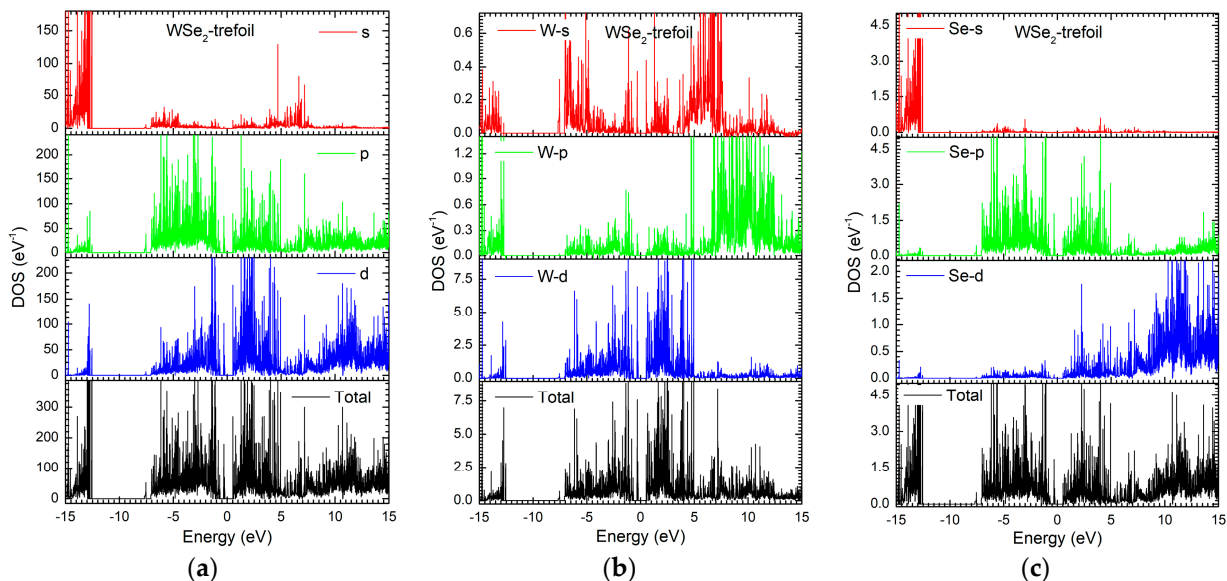


Figure 6. Total and orbital-projected density of states (DOS and PDOS) of trefoil-defective WSe₂: (a) Total orbital-resolved DOS, including the s -, p -, and d -state contributions; (b) W-projected DOS, including the W- s , W- p , and W- d orbital contributions; (c) Se-projected DOS, including the Se- s , Se- p , and Se- d orbital contributions.

Table 2. Calculated band gap values of pristine and trefoil-defective WS₂ monolayers obtained using the DFT + U and SOGGA methods.

Structure	Method	Calculated Band Gap (eV)
Pristine WS ₂ monolayer	DFT + U	1.87
Pristine WS ₂ monolayer	SOGGA	1.96
Trefoil-defective WS ₂ monolayer	DFT + U	1.55
Trefoil-defective WS ₂ monolayer	SOGGA	1.46

The projected DOS demonstrates that the Se 4s orbitals are localized in the deep valence region between approximately -15 and -12 eV, indicating their negligible contribution to the electronic states responsible for charge transport. The Se 4p states dominate the upper valence band and partially contribute to the conduction band through strong hybridization with W 5d orbitals. In contrast, the W 5p orbitals are mainly located at higher energies above approximately 8 eV, while the W 5d states extend continuously across both the valence- and conduction-band edges, highlighting their dominant role in determining the band-edge electronic structure.

The introduction of the trefoil defect significantly reconstructs the electronic spectrum. Compared with pristine WSe₂, the total DOS becomes considerably broader and contains numerous additional electronic states distributed throughout the valence and conduction bands. As a consequence, the forbidden energy region around the Fermi level is substantially narrowed. The calculated band gap decreases to 0.751 eV within DFT + U and 0.645 eV using the SOGGA functional, corresponding to reductions of approximately 51% and 61%, respectively (Table 3).

The pronounced band-gap reduction also shifts the characteristic electronic energy scale of reconstructed WSe₂ toward the near-infrared region. Using $\lambda = hc/E$, the calculated gaps of 0.751 and 0.645 eV correspond to characteristic wavelengths of approximately 1.65 and 1.92 μm , respectively. This suggests that the reconstruction-induced band-edge states may enable lower-energy electronic excitations and may be relevant to defect-engineered near-infrared optoelectronic response. However, these wavelengths should not be interpreted as quantitative optical absorption thresholds, because the calculated values represent electronic DFT band gaps and the present calculations do not explicitly include electron-hole interactions and excitonic effects.

The PDOS analysis reveals that these changes primarily originate from the W 5d orbitals. The spectral weight of the tungsten d states increases markedly in the vicinity of the Fermi level, accompanied by enhanced contributions from the Se 4p orbitals over a broader energy interval. This behavior indicates a pronounced modification of W 5d-Se 4p orbital mixing caused by the local lattice distortion introduced by the trefoil defect. The reduced local symmetry lifts the degeneracy of the electronic states and produces numerous localized defect-induced states close to both band edges. These localized states are responsible for the observed narrowing of the band gap and the increased density of available electronic states near the Fermi level.

To quantify the defect-induced redistribution of the transition-metal d and chalcogen p states, the energy centroids of the corresponding PDOS components were evaluated in the near-valence-band-edge region from -2 to 0 eV relative to the Fermi level. Following the conventional first-moment definition of the PDOS band center [55,56], the centroid energy was calculated as

$$\epsilon_c = \frac{\int_{E_1}^{E_2} ED(E)dE}{\int_{E_1}^{E_2} D(E)dE}, \quad (6)$$

where $D(E)$ is the orbital-projected density of states and the same energy interval was applied to all pristine and reconstructed structures. For pristine WS_2 , the separation between the W $5d$ and S $3p$ centroids is approximately 0.395 eV, whereas in the trefoil-reconstructed structure it decreases to 0.163 eV, corresponding to a reduction of approximately 59%. An even stronger relative change is observed for WSe_2 , where the W $5d$ -Se $4p$ centroid separation decreases from approximately 0.235 eV in the pristine structure to only 0.080 eV after reconstruction, corresponding to a reduction of approximately 66%. Thus, the reconstructed WSe_2 structure exhibits particularly close energetic alignment of the W $5d$ and Se $4p$ states near the valence-band edge. These quantitative results support the defect-induced redistribution and enhanced orbital mixing inferred from the PDOS spectra and provide an electronic contribution to the stronger modification of the band structure observed for WSe_2 .

In contrast, the deep-lying Se $4s$ orbitals remain nearly unchanged after defect formation, indicating that the trefoil defect predominantly affects the chemically active valence orbitals rather than the core-like electronic states. The W $5p$ states also retain their position in the high-energy conduction region, although a moderate broadening of their distribution is observed due to structural relaxation around the defect.

Overall, the DOS and PDOS analyses demonstrate that the electronic properties of WSe_2 are governed by strong hybridization between W $5d$ and Se $4p$ orbitals. The formation of the trefoil defect substantially modifies this hybridization and introduces localized electronic states near the band edges, leading to a pronounced reduction in the band gap.

For pristine WSe_2 , the calculated band gaps are consistent with the energy scale generally obtained using semilocal density-functional approximations. However, these values should not be directly equated with experimental optical-transition energies because monolayer WSe_2 exhibits strong excitonic effects [29]. The much stronger band-gap reduction obtained for reconstructed WSe_2 correlates with its considerably more pronounced structural relaxation. The increase in the mean W-Se bond length, broader bond-length distribution, larger angular distortion, and stronger out-of-plane buckling modify the local orbital environment and the overlap of the W $5d$ and Se $4p$ states. This structural-electronic correlation is consistent with the substantially larger relative band-gap reduction observed for WSe_2 than for WS_2 .

The appearance of additional states near the band edges is also qualitatively consistent with experimental studies showing that local defects in WSe_2 can generate optically active localized states. Moody et al. demonstrated that electron-beam-induced defects in monolayer WSe_2 support defect-bound excitons with recombination lifetimes extending to approximately 200 ns and valley lifetimes exceeding 1 μs [57]. Although these experimentally investigated states were associated with irradiation-induced defects rather than the stoichiometric reconstruction considered here, both studies demonstrate the high sensitivity of the WSe_2 electronic spectrum to local disruption of W-Se coordination.

The stronger response of WSe_2 should therefore not be attributed solely to its smaller pristine band gap. Instead, the present results indicate that it is associated primarily with the stronger local structural relaxation and the accompanying redistribution and enhanced mixing of W $5d$ and Se $4p$ states near the band edges. The greater polarizability of Se $4p$ orbitals may further contribute to this response. Given the presence of heavy W and Se atoms, spin-orbit coupling may also influence the electronic structure; however, its

individual contribution cannot be quantitatively separated from the present calculations and is therefore not assigned a dominant role here.

Table 3. Calculated band gap values of pristine and trefoil-defective WSe₂ monolayers obtained using the DFT + U and SOGGA methods.

Structure	Method	Calculated Band Gap (eV)
Pristine WSe ₂ monolayer	DFT + U	1.533
Pristine WSe ₂ monolayer	SOGGA	1.657
Trefoil-defective WSe ₂ monolayer	DFT + U	0.751
Trefoil-defective WSe ₂ monolayer	SOGGA	0.645

A direct comparison of the two materials reveals that the electronic response to the same nominal reconstruction is strongly chalcogen-dependent. Within DFT + U, the band gap is reduced by approximately 17% in WS₂ and 51% in WSe₂, whereas the corresponding reductions obtained using SOGGA are approximately 26% and 61%, respectively. Thus, the relative electronic effect of the reconstruction is approximately two to three times stronger in WSe₂ than in WS₂.

This contrast correlates directly with the structural data. In WS₂, the reconstruction produces a compensated distribution of shortened and elongated W-S bonds while leaving the mean bond length nearly unchanged. In WSe₂, by contrast, it produces both a broader W-Se bond-length distribution and a net expansion of the local coordination network, together with substantially stronger out-of-plane buckling. The greater geometrical distortion in WSe₂ therefore results in a larger modification of the W 5*d*-chalcogen *p* orbital overlap and a stronger redistribution of electronic states near the band edges.

This interpretation is consistent with previous orbital-resolved first-principles calculations of strained group-VI TMD monolayers. Chang et al. demonstrated that strain-induced changes in metal-chalcogen bond lengths and local coordination modify the orbital composition and positions of the valence- and conduction-band edges in MoS₂, MoSe₂, WS₂, and WSe₂ [58]. In the present systems, the stoichiometric trefoil-like reconstruction can therefore be regarded as a highly localized and nonuniform structural perturbation rather than as a homogeneous strain field.

The much larger electronic response of WSe₂ can therefore be primarily associated with its stronger local geometrical distortion and the accompanying redistribution of W 5*d* and Se 4*p* states near the band edges. The quantitative PDOS-centroid analysis further supports a pronounced defect-induced modification of *d*-*p* orbital mixing, while the specific contribution of spin-orbit coupling remains to be established by dedicated calculations with and without SOC.

4.1. Optical Properties of Pristine and Trefoil-Defective WS₂ Monolayers

The optical absorption spectra of pristine and trefoil-defective WS₂ monolayers were calculated using the DFT + U and SOGGA methods for both in-plane (*x*-*x*/*y*-*y*) and out-of-plane (*z*-*z*) light polarizations (Figure 7). The calculated spectra exhibit pronounced optical anisotropy arising from the layered crystal structure and the anisotropic distribution of the electronic states.

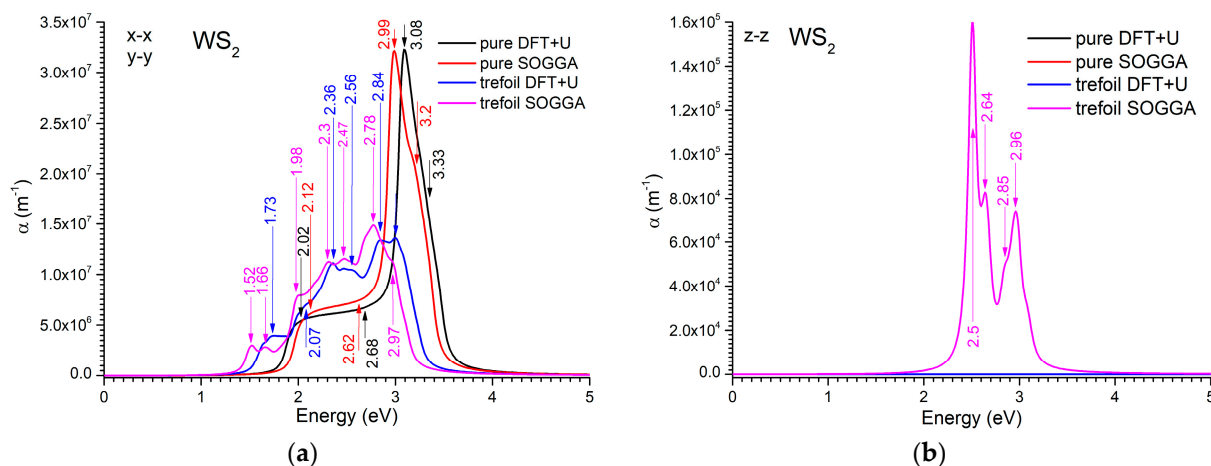


Figure 7. Optical absorption spectra of pristine and trefoil-defective WS₂ monolayers calculated using the DFT + U and SOGGA methods: (a) in-plane polarization (x-x/y-y) and (b) out-of-plane polarization (z-z).

For the in-plane polarization (x-x/y-y), the pristine WS₂ monolayer exhibits a distinct absorption edge near 2.0 eV, followed by an intense absorption maximum located at 3.08 eV within DFT + U and 2.99 eV using the SOGGA functional. The absorption coefficient reaches values exceeding $3 \times 10^7 \text{ m}^{-1}$, indicating efficient interaction with visible light. Additional absorption features appear at 3.33 eV (DFT + U) and 3.20 eV (SOGGA), corresponding to higher-energy interband electronic transitions.

The DOS and PDOS analyses provide insight into the origin of these optical transitions. As shown in Figure 7, the valence-band maximum is mainly formed by hybridized S 3*p* and W 5*d* orbitals, whereas the conduction-band minimum is predominantly composed of W 5*d* states. Therefore, the principal absorption bands of pristine WS₂ originate from electronic transitions between occupied S 3*p*–W 5*d* hybridized states and unoccupied W 5*d* states.

The calculated in-plane absorption edge of pristine WS₂ near 2.0 eV and the higher-energy absorption maximum at approximately 2.99–3.08 eV fall within the energy range in which prominent optical features of monolayer WS₂ are experimentally observed. However, a one-to-one assignment of the calculated peaks to experimental A-, B-, or higher-energy excitonic resonances is not justified within the present computational approach. The Kubo-Greenwood formalism employed here describes independent-particle interband transitions and does not explicitly include the electron-hole attraction. This limitation is important because monolayer WS₂ has an experimentally measured exciton binding energy of $0.71 \pm 0.01 \text{ eV}$ [54].

Accordingly, the calculated absorption features should be interpreted primarily as interband-transition energies and as indicators of relative spectral changes induced by the reconstruction, rather than as quantitative predictions of experimental excitonic peak positions. Within this interpretation, the emergence of additional absorption bands between approximately 1.5 and 2.8 eV provides evidence that the reconstruction activates new low-energy optical channels.

These additional transitions are qualitatively consistent with the general ability of local defects and structural reconstructions in TMD monolayers to generate near-gap states and relax the symmetry-related selection rules of the pristine lattice. In the present system, however, the additional transitions originate from hybridized W 5*d*/S 3*p* states generated by a stoichiometric bond rearrangement rather than from unsaturated orbitals associated with vacancy sites.

The introduction of the trefoil defect substantially modifies the optical response. New absorption peaks emerge in the low-energy region between approximately 1.5 and 2.8 eV, where the pristine monolayer exhibits only weak optical absorption. Within the DFT + U calculations, additional absorption bands appear at 1.73, 2.36, 2.56, 2.84 and 3.0 eV, whereas the SOGGA calculations predict corresponding peaks at 1.52, 1.66, 1.98, 2.3, 2.47, 2.78 and 2.97 eV.

These new optical transitions are directly related to the electronic structure revealed by the DOS calculations. The trefoil defect introduces additional electronic states near both the valence-band maximum and the conduction-band minimum, leading to a pronounced reduction in the electronic band gap. According to the DOS analysis, the band gap decreases from 1.87 to 1.55 eV within DFT + U and from 1.96 to 1.46 eV using the SOGGA functional. The PDOS further demonstrates that these defect-induced states are mainly associated with enhanced hybridization between W *5d* and S *3p* orbitals. The increased density of electronic states near the band edges provides additional initial and final states for interband optical transitions, thereby producing the newly observed low-energy absorption peaks.

Another consequence of the defect formation is the red shift in the principal absorption band. (Here, the term red shift refers to the displacement of the characteristic absorption features toward lower photon energies relative to the corresponding pristine monolayer.) Compared with pristine WS₂, the dominant absorption maximum shifts toward lower photon energies, reflecting the reduced energy separation between the occupied and unoccupied electronic states. Simultaneously, the absorption bands become broader due to the increased number of allowed electronic transitions associated with defect-induced localized states and reduced crystal symmetry.

For the out-of-plane polarization (*z-z*), the calculated absorption spectra differ markedly from those obtained for the in-plane polarization. The maximum absorption coefficient reaches only about $1.6 \times 10^5 \text{ m}^{-1}$, which is approximately two orders of magnitude lower than that for the *x-x/y-y* polarization, confirming the pronounced optical anisotropy of the WS₂ monolayer. A notable methodological difference is observed for the out-of-plane response. Within the DFT + U approach, both pristine and trefoil-defective WS₂ exhibit an almost negligible absorption over the investigated energy range, indicating that optical transitions polarized perpendicular to the monolayer are strongly suppressed. In contrast, the SOGGA calculations predict a pronounced out-of-plane optical response for the trefoil-defective structure, with four distinct absorption peaks located at approximately 2.5, 2.64, 2.82, and 2.92 eV. The appearance of these peaks suggests that the trefoil defect activates additional *z*-polarized interband transitions by locally breaking the crystal symmetry and modifying the orbital hybridization. Therefore, the out-of-plane optical response is found to be strongly dependent on the employed exchange-correlation functional, whereas the in-plane optical spectra remain considerably less sensitive to the computational approach.

The pronounced difference between the in-plane and out-of-plane spectra demonstrates the strong optical anisotropy of monolayer WS₂. This behavior originates from the two-dimensional crystal structure, in which the electronic states responsible for optical transitions are predominantly confined within the basal plane. Consequently, the influence of the trefoil defect is much more pronounced for the in-plane optical response than for the out-of-plane polarization.

Overall, the optical calculations indicate that the trefoil defect modifies the optical response of WS₂ by introducing additional defect-related electronic states near the band edges, increasing the number of available optical transitions, broadening the absorption spectrum, and shifting the absorption edge toward lower photon energies. Together with the DOS and PDOS analyses, these results demonstrate that defect engineering provides an effective route for tuning the electronic and optical properties of WS₂ monolayers.

The pronounced polarization dependence can be related to the defect-induced modification of the W 5*d*-chalcogen *p* electronic states identified in the PDOS analysis. The trefoil reconstruction breaks the local symmetry and modifies the W-X (X = S, Se) coordination, leading to a redistribution and altered energetic alignment of the W 5*d* and chalcogen *p* states near the band edges. These changes modify the available interband transitions and their optical matrix elements, producing a substantially stronger effect on the in-plane (*x*-*x*/*y*-*y*) response. In contrast, the weak variation in the *z*-*z* spectra indicates that the reconstruction does not generate a comparable enhancement of transitions with significant out-of-plane optical matrix elements. The enhanced optical anisotropy can therefore be associated with the polarization-selective consequences of local symmetry breaking and the accompanying modification of W 5*d*-chalcogen *p* orbital mixing.

4.2. Optical Properties of Pristine and Trefoil-Defective WSe₂ Monolayers

The optical absorption spectra of pristine and trefoil-defective WSe₂ monolayers were calculated using the DFT + U and SOGGA methods for both in-plane (*x*-*x*/*y*-*y*) and out-of-plane (*z*-*z*) light polarizations (Figure 8). Similar to WS₂, the calculated spectra demonstrate pronounced optical anisotropy originating from the two-dimensional crystal structure and the anisotropic distribution of the electronic states.

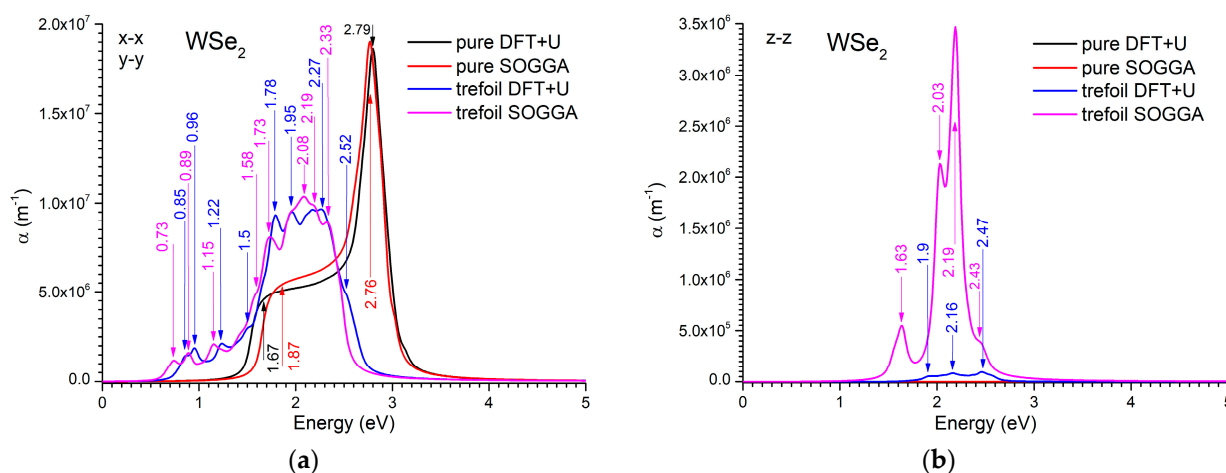


Figure 8. Optical absorption spectra of pristine and trefoil-defective WSe₂ monolayers calculated using the DFT + U and SOGGA methods: (a) in-plane polarization (*x*-*x*/*y*-*y*) and (b) out-of-plane polarization (*z*-*z*).

For the in-plane polarization (*x*-*x*/*y*-*y*), the pristine WSe₂ monolayer exhibits an absorption edge at approximately 1.7–1.9 eV, followed by a strong absorption maximum centered at 2.79 eV for both exchange-correlation functionals. The maximum absorption coefficient reaches approximately $1.9 \times 10^7 \text{ m}^{-1}$, indicating efficient absorption throughout the visible spectral range.

The DOS and PDOS analyses explain the origin of these optical transitions. As discussed in the previous section, the valence-band maximum is mainly composed of hybridized Se 4*p* and W 5*d* orbitals, whereas the conduction-band minimum is predominantly formed by W 5*d* states with a smaller contribution from Se 4*p* orbitals. Consequently, the dominant optical transitions in pristine WSe₂ originate from occupied Se 4*p*-W 5*d* hybridized states to unoccupied W 5*d* states.

The formation of the trefoil defect produces significant modifications in the optical response. Numerous additional absorption peaks appear below the absorption edge of the pristine monolayer. Within the DFT + U calculations, new optical transitions are observed at 0.85, 0.96, 1.22, 1.50, 1.78, 1.95, 2.27, and 2.52 eV, whereas the SOGGA calculations predict

corresponding peaks at 0.73, 0.89, 1.15, 1.58, 1.73, 2.08, 2.19, and 2.33 eV. These additional absorption bands considerably broaden the low-energy part of the spectrum and enhance visible-light absorption.

The appearance of these low-energy optical transitions is in excellent agreement with the calculated electronic structure. The DOS analysis demonstrates that the trefoil defect introduces numerous localized electronic states near both the valence-band maximum and the conduction-band minimum, resulting in a substantial reduction in the electronic band gap. Specifically, the band gap decreases from 1.533 to 0.751 eV within the DFT + U approach and from 1.657 to 0.645 eV using the SOGGA functional. The PDOS further reveals that these defect-induced states originate predominantly from enhanced hybridization between W 5*d* and Se 4*p* orbitals. The increased density of electronic states near the Fermi level provides additional occupied and unoccupied states participating in optical transitions, thereby giving rise to the newly formed low-energy absorption bands.

Another characteristic consequence of the trefoil defect is the pronounced red shift in the optical spectrum. Compared with pristine WSe₂, the dominant absorption features move toward lower photon energies owing to the reduced separation between the valence and conduction bands. In addition, the absorption peaks become considerably broader than those of the pristine monolayer, reflecting the increased number of allowed interband transitions associated with defect-induced localized electronic states and the reduction in crystal symmetry.

The calculated optical response of pristine WSe₂ is broadly consistent with its established strong absorption in the visible spectral range. Nevertheless, the absolute peak positions obtained in the present calculations should be distinguished from experimental excitonic resonances. The experimentally determined exciton binding energy of monolayer WSe₂ is approximately 0.37 eV [29], showing that electron-hole interactions significantly shift the lowest optical resonances below the quasiparticle continuum. The present independent-particle spectra are therefore more reliable for comparing pristine and reconstructed monolayers within the same computational framework than for directly reproducing experimental exciton energies.

The emergence of multiple reconstruction-induced transitions between 0.73 and 2.52 eV is qualitatively consistent with experimental observations that local defects in WSe₂ generate optically active states below the free-exciton energy. Electron-beam-induced defects have been shown to bind excitons and support unusually long recombination and valley lifetimes [57]. These observations support the general conclusion that disruption of the local W-Se coordination environment can extend the optical response of WSe₂ toward lower photon energies.

Nevertheless, the defect-bound excitons observed experimentally in Ref. [59] arise from irradiation-induced defects, whereas the low-energy transitions obtained in the present work originate from a stoichiometric rotational reconstruction. The comparison therefore establishes a common physical trend—the activation of localized or defect-associated low-energy optical channels—but does not imply identical microscopic transition energies, wave functions, or formation mechanisms.

The substantially larger number of low-energy transitions predicted for reconstructed WSe₂ than for WS₂ correlates with the stronger band-gap reduction and the larger spectral weight of W 5*d*/Se 4*p* states near the band edges. The stronger modification of the out-of-plane WSe₂ response, particularly within SOGGA + SOC, further suggests that the pronounced buckling of the Se sublayers activates transitions with finite out-of-plane dipole matrix elements. This interpretation is supported by the structural analysis, according to which the maximum relative thickness increase in reconstructed WSe₂ is more than three times that obtained for WS₂.

The optical response for the out-of-plane polarization (z - z) differs markedly from that observed for in-plane polarization. Although the absorption coefficient remains significantly smaller than that for x - x / y - y polarization, the defect-induced modifications are more pronounced than those observed in WS_2 . In particular, the SOGGA calculations predict intense absorption peaks at approximately 1.63, 2.03, 2.19, and 2.43 eV, while the DFT + U spectra exhibit only relatively weak absorption bands around 1.90, 2.16, and 2.47 eV. This difference indicates that the calculated out-of-plane optical response of WSe_2 is considerably more sensitive to the choice of exchange-correlation functional than that of WS_2 .

Overall, the calculated absorption spectra demonstrate that the trefoil defect strongly modifies the optical properties of monolayer WSe_2 by introducing additional electronic states within the vicinity of the band edges. The enhanced hybridization between W 5d and Se 4p orbitals increases the density of available optical transitions, substantially broadens the absorption spectrum, and shifts the absorption edge toward lower photon energies. These changes extend the optical response into the low-energy visible and near-infrared regions, suggesting that defect engineering provides an effective route for tailoring the optoelectronic characteristics of WSe_2 monolayers for applications in photodetectors, photovoltaics, and other next-generation optoelectronic devices.

Taken together, the present results are consistent with the broader experimental and theoretical understanding of defect engineering in TMD monolayers. Atomic-resolution microscopy and first-principles calculations have shown that threefold rotational defects produce localized structural reconstructions and electronically active states in W-based TMD monolayers [41]. Optical experiments have further demonstrated that local defects in WSe_2 can bind excitons and generate long-lived low-energy optical states [57]. The present calculations show that several related electronic signatures—including the formation of additional band-edge states, band-gap narrowing, and activation of low-energy optical transitions—can also arise from a stoichiometric rotational reconstruction without the removal of atoms.

5. Conclusions

In this work, the influence of a stoichiometric trefoil-like rotational reconstruction on the structural, electronic, and optical properties of WS_2 and WSe_2 monolayers was systematically investigated using DFT + U and SOGGA calculations, with spin-orbit coupling explicitly included in the latter approach. Unlike the experimentally identified chalcogen-deficient $\text{T}_1(3\text{DV})$ defect, the reconstruction considered here was produced through a local 60° bond rotation without removing or adding atoms and therefore preserved the stoichiometric composition of the monolayers.

Structural relaxation revealed a clear material-dependent response. In WS_2 , the reconstruction generated substantial local variations in W-S bond lengths and coordination angles, but the mean W-S distance remained nearly unchanged. This indicates a predominantly local and compensated strain distribution. In contrast, reconstructed WSe_2 exhibited an increase in the mean W-Se bond length from 2.526 to 2.594 Å, a broader and more asymmetric bond-length distribution, and considerably stronger out-of-plane relaxation. These results demonstrate that WSe_2 is structurally more compliant under local rotational reconstruction.

The structural distortions strongly affected the electronic states near the band edges. The DOS and PDOS analyses showed that the reconstruction predominantly modifies hybridized W 5d and chalcogen p states, whereas the deeper chalcogen s states remain almost unaffected.

The calculated absorption spectra exhibited pronounced polarization dependence. For both materials, the in-plane optical response was considerably stronger than the out-of-plane response, reflecting the predominantly planar character of the band-edge orbitals. The rotational reconstruction produced a red shift in the absorption edge, broadened the optical spectra, and activated additional low-energy interband transitions.

The consistency of the qualitative trends predicted by DFT + U and SOGGA supports the conclusion that band-gap narrowing and the activation of low-energy optical channels are robust consequences of the stoichiometric trefoil-like reconstruction.

Overall, the results establish a direct relationship between local structural reconstruction, $W 5d$ –chalcogen p hybridization, band-edge modification, and polarization-dependent optical absorption. The much stronger response of WSe_2 indicates that the chemical identity of the chalcogen plays a decisive role in determining the sensitivity of tungsten-based TMD monolayers to topological bond rearrangements. Stoichiometric rotational reconstruction may therefore provide a route for extending and tuning the spectral response of atomically thin TMDs. Therefore, the present results should primarily be regarded as theoretical trends describing the response of the electronic structure and optical spectra to local rotational reconstruction rather than as quantitative predictions of device-level performance. Nevertheless, formation-energy calculations, spatially resolved electronic-state analysis, excitonic calculations, and evaluation of carrier recombination and transport are required before any improvement in practical optoelectronic device performance can be established.

Author Contributions: Conceptualization, D.S., methodology, D.S.; software, D.S. and G.S.; validation, D.S. and A.D.; formal analysis, D.S. and G.S.; investigation, D.S., G.S. and A.D.; resources, D.S.; data curation, D.S.; writing—original draft preparation, D.S.; writing—review and editing, D.S. and G.S.; visualization, D.S. and G.S.; supervision, D.S.; project administration, D.S.; funding acquisition, D.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research has been funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No. AP23488734).

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding authors.

Acknowledgments: During the preparation of this manuscript/study, the authors used ChatGPT (GPT-5.6 Sol, OpenAI) for the purposes of assisting with translation from Kazakh into English and to improve English grammar, wording, and stylistic clarity. The authors have reviewed and edited the output and take full responsibility for the content of this publication.

Conflicts of Interest: The authors declare no conflicts of interest.

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