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Research Paper

Influence of van der Waals Interactions on the Structural and Electronic Characteristics of SnSe: A DFT-Based Analysis

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ABSTRACT

Layered SnSe has attracted substantial interest due to its promising electronic and thermoelectric properties, which are strongly influenced by its anisotropic crystal structure. In this study, we systematically investigate the effects of van der Waals (vdW) interactions on the structural and electronic properties of SnSe by comparing first-principles calculations performed with and without the DFT-D3 correction. Structural relaxation results show that the inclusion of vdW interactions slightly reduces the interlayer spacing and the lattice parameter a, while the intralayer Sn–Se bond lengths remain nearly unchanged, reflecting the dominance of covalent bonding within the layers. Electronic band structure calculations reveal that SnSe maintains its indirect band gap of approximately 0.56–0.57 eV in both cases, with negligible shifts in the valence band maximum and conduction band minimum. Furthermore, the projected density of states (PDOS) confirms that the dominant orbital contributions—Sn 5p and Se 4p in the valence band and Sn 5p in the conduction band—are unaffected by the vdW correction. These findings indicate that while vdW interactions are essential for accurately describing the structural geometry of layered SnSe, they have limited influence on its intrinsic electronic characteristics. This work provides valuable insights for future theoretical and experimental studies aimed at optimizing SnSe-based electronic and thermoelectric applications.

Keywords: SnSe; van der Waals correction; DFT-D3; electronic band structure; projected density of states; lattice parameters; first-principles calculation

INTRODUCTION

Tin selenide (SnSe) has gained considerable attention as a high-performance chalcogenide material due to its exceptional thermoelectric efficiency, anisotropic transport behavior, and rich electronic properties (1,2). Its orthorhombic layered structure, held together by relatively weak interlayer interactions, makes SnSe highly relevant for applications in two-dimensional devices, optoelectronics, and energy conversion technologies (3,4). However, this layered nature also presents notable challenges for theoretical modeling. Conventional density functional theory (DFT) methods often struggle to accurately capture the long-range dispersion forces responsible for interlayer cohesion (5,6). As a result, structural predictions such as lattice constants, interlayer spacing, and subtle atomic displacements may deviate from experimental values when van der Waals (vdW) interactions are not explicitly accounted for (7,8).

To address this limitation, modern DFT studies commonly incorporate a specific vdW correction scheme that enhances the description of dispersion forces. In the case of SnSe, including such a correction is particularly important because its electronic structure is highly sensitive to geometric changes. Small variations in lattice parameters can shift the valence and conduction bands, modify the band gap, and alter orbital contributions reflected in the projected density of states (PDOS) (9,10). Consequently, the use of vdW corrections is expected to influence not only the optimized geometry but also the resulting band structure and electronic characteristics.

Despite the recognized importance of vdW interactions in layered materials, systematic studies comparing the structural and electronic properties of SnSe with and without a single, well-defined vdW correction remain limited (11,12). Most existing reports focus either on structural optimization or electronic behavior independently, leaving a gap in understanding how vdW-induced geometric changes translate into modifications in the band structure and PDOS. A consistent and direct comparison is therefore essential to evaluate the extent to which dispersion corrections influence predictive accuracy and whether standard functionals such as PBE are sufficient for describing SnSe when vdW effects are neglected (13,14).

In this work, we aim to provide a comprehensive analysis of SnSe by performing DFT calculations under two conditions: (i) without any vdW correction and (ii) with one selected vdW correction scheme applied consistently. By comparing the resulting lattice parameters, band structures, and PDOS, this study seeks to reveal how the inclusion of vdW interactions affects both the structural and electronic properties of SnSe. The findings are expected to guide researchers in choosing appropriate computational methods for layered chalcogenides and contribute to a deeper understanding of structure–property relationships in SnSe.

COMPUTATIONAL METHODOLOGY

All first-principles calculations were carried out using the Quantum ESPRESSO package based on density functional theory (DFT). The exchange–correlation interactions were treated within the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) functional. To describe the core–valence interactions accurately, we employed projector augmented-wave (PAW) pseudopotentials. Because SnSe is a layered material with weak interlayer interactions, van der Waals forces were included using the DFT-D3 semi-empirical dispersion correction throughout the calculations that require vdW treatment.

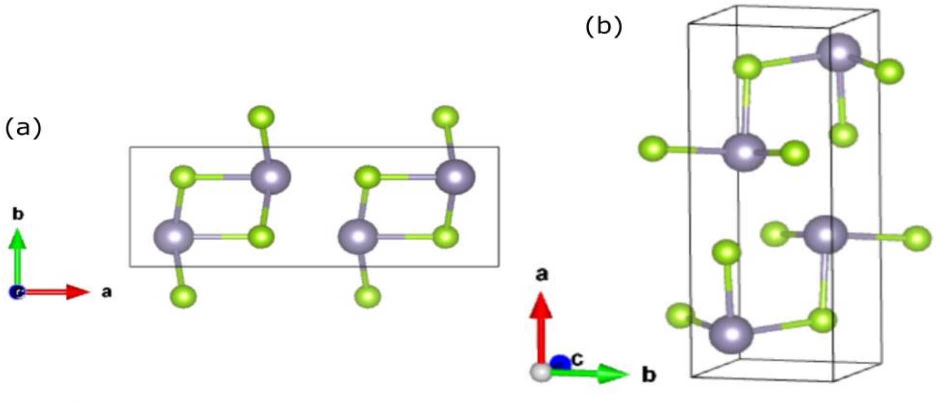

Figure 1. Top and side views of the orthorhombic SnSe crystal structure. The layered arrangement of Sn and Se atoms along the a-axis is clearly visible, highlighting the weak interlayer interaction and strong intralayer Sn–Se bonding.

The initial orthorhombic crystal structure of SnSe was optimized to obtain the equilibrium lattice parameters and relaxed atomic positions. A plane-wave basis set with a kinetic-energy cutoff (ecutwfc) of 60 Ry and a charge-density cutoff (ecutrho) of 480 Ry was adopted to ensure well-converged total energies and forces. Brillouin-zone integrations for the structural optimization and ground-state calculations were performed using a 4 × 12 × 12 Monkhorst–Pack k-point grid, which provided sufficient sampling along the anisotropic directions of the crystal.

For the electronic structure analysis, two types of calculations were performed. The projected density of states (PDOS) was computed using a denser 8 × 24 × 24 k-point grid to achieve accurate orbital projections and smooth DOS profiles. Meanwhile, the band-structure calculation employed a non-self-consistent field (NSCF) procedure along a selected high-symmetry path in the Brillouin zone. The chosen path follows Γ – X – S – Y – Γ – Z – U – R – T – Z, which captures the key dispersive features of SnSe along both in-plane and out-of-plane directions.

Figure 1 presents the top view and side view of the SnSe crystal, highlighting its layered arrangement and anisotropic bonding environment. These structural motifs are essential for understanding the sensitivity of SnSe to vdW corrections. All calculations were iterated until the total energy change was below the required convergence threshold, and structural relaxations were considered converged when the residual forces on each atom were below 10^{-3} Ry/Bohr. The combination of PAW pseudopotentials, GGA-PBE functional, and DFT-D3 correction provides a reliable framework for evaluating the effects of dispersion interactions on the lattice parameters, band structure, and PDOS of SnSe.

RESULT AND DISCUSSION

The structural optimization results of SnSe obtained with and without the DFT-D3 van der Waals correction reveal meaningful differences in both lattice parameters and Sn–Se bond lengths. As summarized in Table 1, incorporating vdW dispersion forces leads to a consistent contraction of the lattice constants *a*, *b*, and *c*. The most pronounced reductions occur along the *b* axis (−0.72%) and the *a* axis (−0.58%), while the *c* axis experiences only a very small contraction (−0.16%). This behavior indicates that the vdW correction strengthens the overall attractive interactions within the structure, resulting in a slightly more compact equilibrium geometry.

Table 1. Structural parameters of SnSe obtained from DFT calculations without and with the DFT-D3 van der Waals correction

Parameter	Without vdW (Å)	With vdW (Å)
a	11.51123	11.44482
b	4.19031	4.16026
c	4.44764	4.44031
l_{12}	2.77259	2.77556
l_{13}	2.82010	2.80555
d (interlayer)	2.71350	2.64996

More importantly, the inclusion of the DFT-D3 correction affects the Sn–Se bond lengths, denoted as l_{12} and l_{13}. These two bond lengths correspond to distinct Sn–Se bonding directions within the puckered layers of SnSe. l_{12} exhibits a small increase from 2.77259 Å to 2.77556 Å (+0.11%), suggesting a mild stretching of this specific Sn–Se bond. In contrast, l_{13} shows a decrease from 2.82010 Å to 2.80555 Å (−0.52%), indicating a slight strengthening or tightening of the corresponding Sn–Se interaction. These opposite trends reflect the intrinsic anisotropy of the SnSe lattice:

because the structure consists of strongly bonded Sn–Se units arranged in a puckered configuration, dispersion corrections can modify the internal relaxation pattern differently for each distinct Sn–Se bond orientation. Such anisotropic adjustments are consistent with the bonding environment visible in the top and side views of the structure (Figure 1).

The parameter *d*, which characterizes the overall interlayer separation, shows the largest relative change (−2.34%), confirming that vdW forces strongly influence the weak interactions between adjacent layers. The significant contraction of *d* is consistent with the expected physical effect of including long-range dispersion forces in layered materials. These structural modifications, particularly changes in Sn–Se bond lengths and interlayer spacing, are expected to influence the electronic structure, as both the band dispersion and PDOS of SnSe are sensitive to subtle geometric variations. Therefore, the structural differences observed here must be carefully considered when interpreting the corresponding electronic results.

The calculated band structures of SnSe without and with the DFT-D3 van der Waals correction are shown in Figure 2. Both band structures reveal that SnSe maintains an indirect band-gap character along the selected high-symmetry path. In the case without vdW correction (Figure 2 (a)), the band gap is found to be approximately 0.57 eV, with the valence band maximum (VBM) located slightly away from the Γ point and the conduction band minimum (CBM) occurring near the same region but at a different k-point. When the vdW correction is included (Figure 2 (b)), the band gap slightly decreases to 0.56 eV, demonstrating that the dispersion correction has only a minor influence on the overall electronic band-gap magnitude.

Even though the band-gap difference is small, careful inspection of the two band structures reveals subtle modifications in the dispersion of both conduction and valence bands. These changes are mainly observed in regions associated with interlayer interactions, such as the Z–U–R and T–Z segments. This behavior is consistent with the structural analysis, where vdW correction was shown to reduce the interlayer distance significantly. The slight increase in interlayer coupling introduced by the vdW term results in modest adjustments to the curvature and relative positions of bands, particularly in directions normal to the SnSe layers. However, the essential topology of the electronic structure, such as the indirect nature of the gap, the bandwidths of the valence states, and the clustering of conduction bands, remains largely unchanged, indicating that the primary Sn–Se bonding states are not substantially altered by the vdW correction.

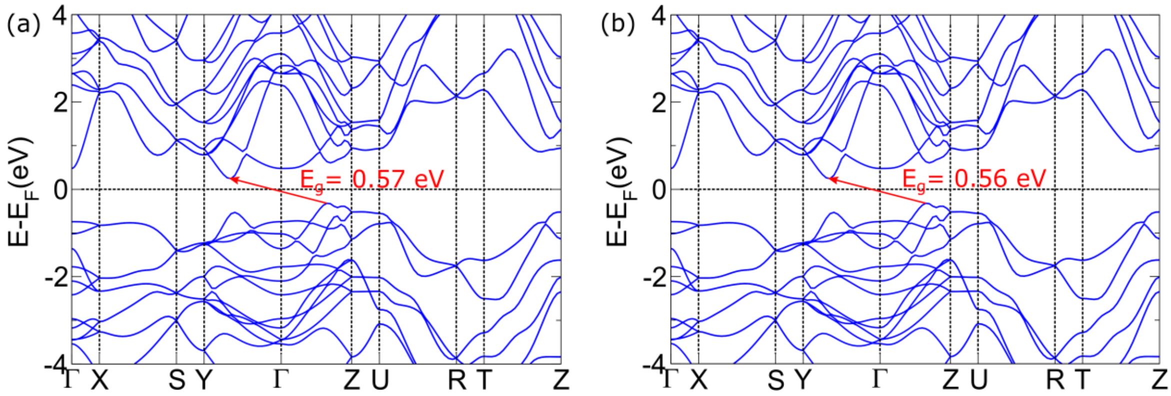

Figure 2. Electronic band structures of SnSe calculated using GGA-PBE (a) without and (b) with the DFT-D3 van der Waals correction along the high-symmetry path Γ–X–S–Y–Γ–Z–U–R–T–Z.

Overall, the results confirm that while vdW interactions play an important role in determining the equilibrium geometry of layered SnSe, their impact on the electronic band gap is relatively small within the GGA-PBE framework. This suggests that the electronic properties of SnSe are primarily governed by strong intralayer Sn–Se bonding, with vdW effects contributing only secondary corrections to interlayer-dominated features in the band structure. These findings provide a consistent picture when compared with the structural results, reinforcing the importance of vdW corrections for accurate lattice representation but highlighting their limited influence on the fundamental electronic gap.

The projected density of states (PDOS) of SnSe calculated without and with the DFT-D3 van der Waals correction is shown in Figure 3. In both cases, the electronic states near the Fermi level are dominated by the hybridization between Sn 5p and Se 4p orbitals, which form the valence band maximum (VBM) and conduction band minimum (CBM). The PDOS profiles demonstrate that the strong covalent character of the Sn–Se bonds is preserved regardless of the inclusion of vdW corrections, consistent with the earlier observation that vdW interactions mainly influence the interlayer structure rather than intralayer bonding.

In the occupied region, the valence band from approximately –6 eV to 0 eV is primarily composed of contributions from Se 4p orbitals, with Sn 5p states providing a secondary but noticeable contribution. A slightly deeper energy region (around –9 to –6 eV) is dominated by Sn 5s states, appearing as a distinct peak in both calculations. The similarities in the distribution and intensity of these states between Figures 3a and 3b indicate that the vdW correction does not significantly perturb the bonding environment or local electronic configuration of SnSe.

In the unoccupied region above the Fermi level, the conduction bands show strong involvement of Sn 5p states, accompanied by moderate contributions from Se 4p states. The overall shape and relative intensity of the conduction band PDOS peaks remain nearly identical between the two calculations. This further supports the conclusion that the dominant electronic structure of SnSe—defined primarily by strong intralayer Sn–Se covalency—is largely unaffected by vdW interactions. Because vdW forces act mainly between layers, their influence appears in structural relaxation rather than in altering the electronic states associated with directional Sn–Se bonds.

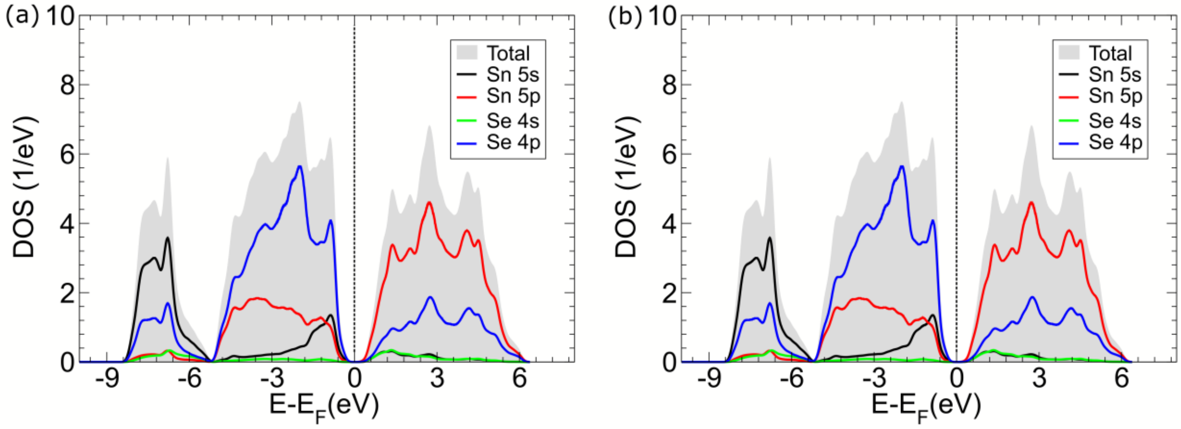

Figure 3. Projected density of states (PDOS) of SnSe calculated using GGA-PBE (a) without and (b) with the DFT-D3 van der Waals correction. Shaded regions represent the total DOS, while colored curves show orbital-resolved contributions from Sn 5s, Sn 5p, Se 4s, and Se 4p states.

Although the inclusion of vdW corrections does not cause major changes in the PDOS, slight redistributions in peak sharpness and intensity can be observed across the valence and conduction bands. These small variations arise from the subtle modifications in interlayer spacing induced by DFT-D3, which may slightly adjust the overlap between orbitals in directions perpendicular to the layers. However, these effects are minor and do not lead to meaningful shifts in energy levels or changes in orbital character across the studied energy range. Overall, the PDOS analysis confirms that the electronic structure of SnSe is robust against vdW corrections, consistent with the band structure results. The dominant Sn 5p–Se 4p hybridization governs the electronic properties near the band edges, while vdW interactions contribute only minor adjustments without altering the fundamental electronic characteristics of the material.

CONCLUSION

This study demonstrates that including van der Waals (vdW) correction using DFT-D3 affects the structural properties of SnSe but has only a minimal impact on its electronic characteristics. The vdW interaction slightly reduces the lattice parameter a and the interlayer distance, confirming its role in strengthening interlayer attraction, while the intralayer Sn–Se bond lengths (l_{12} and l_{13}) remain essentially unchanged due to strong covalent bonding within the layers. The electronic band structure shows that SnSe retains an indirect band gap of about 0.56–0.57 eV in both calculations, with negligible shifts in the VBM and CBM positions. This indicates that interlayer interactions modified by vdW do not significantly alter the intrinsic electronic behavior of SnSe. The PDOS analysis further supports this conclusion: the valence bands are dominated by Sn 5p and Se 4p hybridization, while the conduction bands arise mainly from Sn 5p states, with no meaningful differences between calculations with and without vdW correction. Overall, the vdW correction is important for accurately describing the structural geometry of layered SnSe but does not substantially modify its fundamental electronic properties.

Declaration by Authors

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