FIRST-PRINCIPLES INVESTIGATION OF THE ELECTRONIC PROPERTIES OF MONOLAYER MOSE₂

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Abstract

Monolayer molybdenum diselenide ($MoSe_2$), a notable two-dimensional transition metal dichalcogenide, has garnered significant attention for its favorable electronic structure and potential applications in optoelectronic and photovoltaic-related fields. In this work, the intrinsic electronic properties of monolayer $MoSe_2$ are systematically investigated using first-principles calculations based on density functional theory. The electronic band structure and total density of states are calculated to provide a comprehensive description of the fundamental electronic behavior of the material. The results indicate that monolayer $MoSe_2$ is a direct band-gap semiconductor, with both the valence band maximum and the conduction band minimum located at the K point of the Brillouin zone. The calculated band gap is consistent with previously reported theoretical results, confirming the reliability of the computational methods employed. Analysis of the band dispersion reveals relatively flat valence bands and more dispersive conduction bands near the K point, suggesting distinct effective masses for holes and electrons. Furthermore, the density of states analysis shows that the electronic states near the band edges are predominantly contributed by Mo-d and Se-p orbitals, highlighting the key role of orbital hybridization in determining the electronic structure. Overall, this study provides a clear and consistent understanding of the electronic properties of monolayer $MoSe_2$ and offers a useful theoretical reference for future investigations of two-dimensional transition metal dichalcogenides and their optoelectronic-related applications.

Keywords: *Monolayer $MoSe_2$; Two-dimensional materials; Transition metal dichalcogenides; Density functional theory; Electronic band structure; Density of states.*

Nghiên cứu các tính chất điện tử của đơn lớp $MoSe_2$ bằng phương pháp từ nguyên lý đầu tiên

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Tóm tắt

Molypden diselenide đơn lớp ($MoSe_2$), một đại diện tiêu biểu của nhóm vật liệu hai chiều thuộc họ chalcogenide kim loại chuyển tiếp, đã thu hút nhiều sự quan tâm nhờ cấu trúc điện tử thuận lợi và tiềm năng ứng dụng trong các lĩnh vực quang - điện tử và liên quan đến pin mặt trời. Trong công trình này, các tính chất điện tử nội tại của đơn lớp $MoSe_2$ được khảo sát một cách có hệ thống bằng phương pháp tính toán từ nguyên lý đầu tiên dựa trên lý thuyết phiếm hàm mật độ. Cấu trúc vùng năng lượng và mật độ trạng thái tổng được tính toán nhằm mô tả toàn diện hành vi điện tử cơ bản của vật liệu. Kết quả cho thấy đơn lớp $MoSe_2$ là một chất bán dẫn có vùng cấm trực tiếp, với đỉnh vùng hóa trị và đáy vùng dẫn đều nằm tại điểm K trong vùng Brillouin. Giá trị vùng cấm tính toán phù hợp với các kết quả lý thuyết đã được công bố trước đó, qua đó, khẳng định độ tin cậy của phương pháp tính toán được sử dụng. Phân tích độ phân tán của các dải năng lượng cho thấy các dải hóa trị tương đối phẳng trong khi các dải dẫn có độ phân tán lớn hơn gần điểm K, gợi ý sự khác biệt về khối lượng hiệu dụng của lỗ trống và điện tử. Ngoài ra, phân tích mật độ trạng thái cho thấy các trạng thái điện tử gần mép vùng chủ yếu bắt nguồn từ các orbital Mo-d và Se-p, nhấn mạnh vai trò quan trọng của sự lai hóa orbital trong việc quyết định cấu trúc điện tử của vật liệu. Tóm lại, nghiên cứu này cung cấp một cái nhìn rõ ràng và nhất quán về các tính chất điện tử của đơn *lớp $MoSe_2$, đồng thời, đóng vai trò như một tài liệu tham khảo lý thuyết hữu ích cho các nghiên cứu trong tương lai về vật liệu hai chiều thuộc họ chalcogenide kim loại chuyển tiếp và các ứng dụng liên quan đến quang - điện tử.*

Từ khóa: *Vật liệu hai chiều, Chalcogenide kim loại chuyển tiếp, lý thuyết phiếm hàm mật độ, cấu trúc vùng năng lượng điện tử, mật độ trạng thái.*

Introcdution

Two-dimensional (2D) materials have attracted sustained interest over the past two decades due to their distinctive electronic and optical properties arising from reduced dimensionality [1]-[3]. Quantum confinement of charge carriers in atomically thin layers leads to modified electronic band structures and enhanced light-matter interactions compared with bulk materials [4]. These unique characteristics make 2D materials promising platforms for exploring novel physical phenomena and for developing next-generation optical and optoelectronic devices [5]. Graphene, as the first isolated 2D material, exhibits exceptional carrier mobility and broadband optical absorption [6]. However, the absence of an intrinsic band gap significantly limits its direct application in semiconductor-based optical and optoelectronic technologies [7]. This limitation has motivated extensive research efforts toward identifying alternative 2D materials with finite band gaps and favorable optical properties [8], [9].

Among the various families of 2D materials, transition metal dichalcogenides (TMDs) with the chemical formula MX_2 (M = Mo, W; X = S, Se, Te) have emerged as particularly attractive candidates [10-11]. These materials possess a layered crystal structure consisting of a transition metal layer sandwiched between two chalcogen layers and held together by weak van der Waals interactions [12]. Such a structure enables the fabrication of stable monolayers via mechanical exfoliation or chemical vapor deposition [13]. Importantly, many semiconducting TMDs exhibit a thickness-dependent evolution of their electronic properties, undergoing a transition from an indirect band gap in the bulk to a direct band gap in the monolayer limit [14-15]. This transition leads to significantly enhanced optical absorption and photoluminescence efficiency, making monolayer TMDs highly suitable for optical and optoelectronic applications [16], [17].

Molybdenum diselenide ($MoSe_2$) is a representative semiconducting TMD that has attracted increasing attention due to its favorable electronic structure and strong interaction with light in the visible and near-infrared spectral regions [18-19]. In its monolayer form, $MoSe_2$ exhibits a direct band gap located at the K point of the Brillouin zone, which enables efficient optical transitions without phonon assistance [20]. Compared with other commonly studied TMDs such as MoS_2, monolayer $MoSe_2$ possesses a relatively smaller band gap, extending its optical response toward longer wavelengths [21]. These characteristics suggest that $MoSe_2$ is a promising candidate for ultrathin photonic and optoelectronic devices, including photodetectors, light-emitting devices, and solar-energy-related optical components [22]. From the perspective of optical applications, a detailed understanding of the electronic band structure and density of states is of fundamental importance, as these properties directly govern optical transition energies, absorption spectra, and carrier dynamics [23]. In particular, the nature of the band gap, the dispersion of electronic bands, and the orbital contributions near the band edges play crucial roles in determining the optical response of 2D semiconductors [24]. First-principles calculations based on density functional theory provide a powerful theoretical framework for investigating these intrinsic electronic properties and establishing structure-property relationships in two-dimensional materials [25-26].

In this work, we present a systematic first-principles investigation of the electronic band structure and density of states of monolayer $MoSe_2$ using density functional theory. The present study focuses on the intrinsic electronic properties without considering spin-orbit coupling, aiming to provide a clear and consistent description of the fundamental electronic features relevant to optical behavior. The results obtained in this work offer valuable theoretical insights into the electronic structure of monolayer $MoSe_2$ and serve as a useful reference for future theoretical and experimental studies of two-dimensional transition metal dichalcogenides in optical and optoelectronic applications.

2. Computational Method

2.1. Density Functional Theory

All first-principles calculations in this work were carried out within the framework of density functional theory (DFT) using the Vienna *Ab initio* Simulation Package (VASP) [27-28]. The interaction between valence electrons and ionic cores was described by the projector augmented-wave (PAW) method [29]. A plane-wave basis set was employed, and a sufficiently large vacuum region of approximately 15-20 Å was introduced along the out-of-plane direction to eliminate spurious interactions between periodically repeated layers, ensuring the two-dimensional nature of the monolayer system.

The Brillouin zone integration was performed using a Monkhorst-Pack *k*-point sampling scheme [30]. Convergence tests were carried out to ensure that the calculated electronic properties were independent of the chosen computational parameters.

2.2. Exchange-Correlation Functional

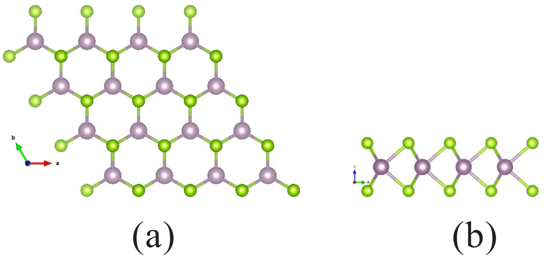
The exchange-correlation effects were treated within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional [31]. This functional has been widely employed in previous first-principles studies of transition metal dichalcogenides and provides a reliable qualitative description of their electronic band structures [32]. The plane-wave energy cutoff was chosen according to convergence tests to ensure accurate evaluation of the electronic structure.

3. Results and Discussion

3.1 Crystal Structure of Monolayer $MoSe_2$

Monolayer $MoSe_2$ crystallizes in a hexagonal structure with trigonal prismatic coordination, belonging to the $P\bar{6}m2$ space group. Each molybdenum atom is coordinated by six selenium atoms, forming a Se-Mo-Se sandwich-like structure [5,21].

Figure 1: Top-view (a) and (b) Side-view of the Optimized Crystal Structure of Monolayer $MoSe_2$.



(a) (b)

The optimized lattice parameters obtained in this work are consistent with previously reported theoretical and experimental values [8,22,34], indicating that the adopted computational approach provides a reliable description of the structural properties.

3.2. Electronic Band Structure

The electronic band structure of monolayer $MoSe_2$ calculated is shown in Figure 2. The results indicate that monolayer $MoSe_2$ is a direct band-gap semiconductor, with both the valence band maximum and conduction band minimum located at the K point of the Brillouin zone. This feature is a well-known characteristic of monolayer transition metal dichalcogenides [8,9,34].

Figure 2. Electronic band structure of monolayer $MoSe_2$

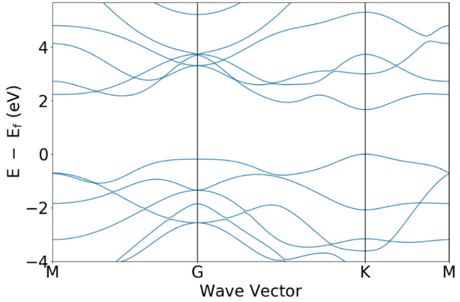


Figure 2 presents the calculated electronic band structure of monolayer $MoSe_2$ along the high-symmetry path M-Γ-K-M in the Brillouin zone, with the Fermi level set to zero energy. The band structure clearly indicates that monolayer $MoSe_2$ is a direct band-gap semiconductor, as both the valence band maximum (VBM) and the conduction band minimum (CBM) are located at the K point. This direct band-gap nature is a well-known characteristic of monolayer transition metal dichalcogenides and distinguishes them from their bulk counterparts, which typically exhibit indirect band gaps. The absence of electronic bands crossing the Fermi level further confirms the intrinsic semiconducting behavior of monolayer $MoSe_2$.

A closer examination of the band dispersion reveals that the valence bands near the K point exhibit relatively weak dispersion, implying a larger effective mass for holes, which may affect hole transport properties. In contrast, the conduction bands show stronger dispersion, particularly around the K point, indicating smaller electron effective masses and potentially higher electron mobility. The smooth and continuous evolution of the bands throughout the Brillouin zone reflects the underlying crystal symmetry and the hybridization between atomic orbitals in the monolayer structure. No band splitting is observed near the band edges, which is consistent with calculations performed without the inclusion of spin-orbit coupling.

The calculated band gap is approximately 1.44 eV, which agrees well with previously reported first-principles results obtained using similar exchange-correlation functionals, confirming the reliability of the present computational approach [9,34]. In addition, the clear energy separation between the band edges at the K point and those at other high-symmetry points, such as Γ, further emphasizes the direct-gap character of monolayer $MoSe_2$. This direct band-gap feature is particularly favorable for optical transitions, as it enables efficient electron-hole excitation without phonon assistance, thereby enhancing light absorption and emission efficiency. Overall, the calculated band structure provides a reliable description of the fundamental electronic properties of monolayer $MoSe_2$ and forms a solid basis for further investigations of its optical and optoelectronic behavior.

3.3. Density of States

The total and partial density of states (DOS) of monolayer $MoSe_2$ are presented in Figure 3.

Figure 3. Total and partial density of states of monolayer $MoSe_2$

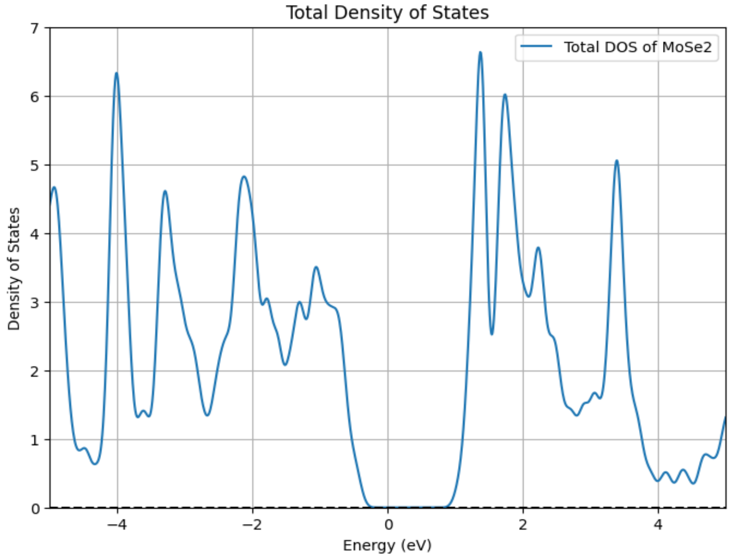
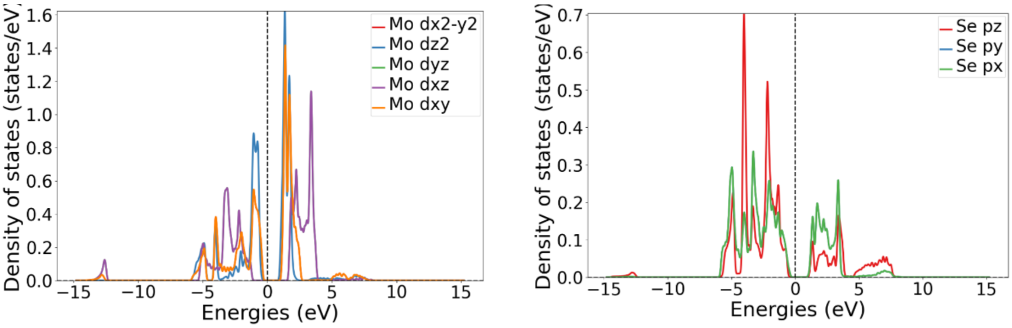


Figure 3 shows the calculated total density of states (DOS) of monolayer $MoSe_2$, with the Fermi level set to zero energy. A well-defined energy gap with vanishing DOS is clearly observed around the Fermi level, which further confirms the semiconducting nature of monolayer $MoSe_2$, in agreement with the band structure results. The presence of this finite band gap indicates the absence of available electronic states at the Fermi level and reflects the intrinsic electronic stability of the monolayer system.

In the valence band region below the Fermi level, several pronounced DOS peaks are observed, indicating a high density of occupied electronic states associated with bonding interactions. These peaks arise from the contributions of specific atomic orbitals and reflect the complex electronic structure of the material. In contrast, the conduction band region above the Fermi level exhibits distinct DOS features corresponding to unoccupied electronic states that become accessible upon electronic excitation. The asymmetric distribution of the DOS between the valence and conduction bands suggests different orbital characters and bonding environments near the band edges. Overall, the DOS results are fully consistent with the calculated band structure and provide complementary insight into the electronic characteristics of monolayer $MoSe_2$.

Figure 4. Projected density of states of monolayer $MoSe_2$ resolved into Mo *d* and Se *p* orbitals



The DOS analysis reveals that the electronic states near the valence band edge are mainly dominated by Mo *d* orbitals with additional contributions from Se *p* orbitals, whereas the conduction band edge is primarily composed of Mo d states, as shown in Figure 4. The results show that the electronic states near the valence band maximum are dominated by Mo *d* states with noticeable contributions from Se *p* orbitals, indicating strong hybridization between Mo and Se atoms. In contrast, the conduction band region is primarily governed by Mo *d* orbitals. This resolved orbital analysis confirms that Mo *d* - Se *p* hybridization plays a key role in determining the electronic structure near the band edges of monolayer $MoSe_2$ These orbital characteristics are consistent with previously reported first-principles studies on Mo-based TMDs [33-34].

3.4. Comparison with Previous Studies

The present calculations confirm that monolayer $MoSe_2$ is a direct band-gap semiconductor with both the valence band maximum and the conduction band minimum located at the K point of the Brillouin zone. This result is in good agreement with previous first-principles studies reported in the literature [8,9,25,31,39], which have consistently identified the direct-gap nature of monolayer $MoSe_2$. The calculated band gap value obtained in this work is comparable to those reported in earlier theoretical investigations. Minor discrepancies in the band gap values among different studies can be reasonably attributed to variations in the choice of exchange-correlation functional, pseudopotentials, K-point sampling, and other computational parameters. Generalized gradient approximation-based calculations are known to slightly underestimate band gap values compared with more advanced approaches. Nevertheless, the overall electronic features, including the location of the band edges and the general band dispersion, remain consistent across different studies. These observations confirm the reliability of the present computational approach and support the validity of the calculated electronic properties of monolayer $MoSe_2$.

4. Conclusion

In summary, a comprehensive first-principles analysis has been carried out to elucidate the intrinsic electronic characteristics of monolayer $MoSe_2$. The calculated electronic band dispersion confirms the presence of a direct energy gap at the K point, while the absence of electronic states at the Fermi level consistently reflects the semiconducting nature of the monolayer system. The distinct dispersion behaviors of the valence and conduction bands further suggest asymmetric carrier transport characteristics for holes and electrons, which are relevant to charge dynamics in low-dimensional semiconductors. The density of states analysis provides additional insight into the microscopic origin of the electronic structure, revealing that the band-edge states are primarily governed by hybridized Mo *d* and Se *p* orbitals. This orbital composition underpins the observed band-gap characteristics and plays a key role in determining the optical transition behavior of monolayer $MoSe_2$. The strong agreement between this study and earlier theoretical investigations validates the computational methods employed.

From an application perspective, the direct band gap and favorable electronic features identified in this work highlight the potential of monolayer $MoSe_2$ as an active material for optical and optoelectronic devices, such as ultrathin photodetectors and light-absorbing components in next-generation energy-related technologies. The findings presented here establish a solid theoretical foundation for further investigations, including the effects of external perturbations, heterostructure engineering, and advanced optical phenomena in two-dimensional transition metal dichalcogenides.

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