Quasiparticle electronic structure of 1T’-MoS₂ within GW approximation

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Abstract. Two-dimensional transition metal dichalcogenides, such as MoS₂, exhibit several polymorphs, namely semiconducting 1H, metallic 1T, and semi-metallic 1T’. Recent experiment [Xinmao Yin et al., Nat. Commun. 8, 486 (2017)] showed an inverted gap of 0.5 eV and a fundamental gap of 0.1 eV in the absorption spectrum of the semi-metallic 1T’-MoS₂. We carry out first-principles calculations on the electronic band structure of 1T’-MoS₂. Since the transition across the fundamental gap occurs at a non-high-symmetry k-point, the choice of k-point sampling is crucial. Our converging result regarding k-point sampling shows that two bands touch at Fermi energy. It indicates the absence of fundamental gap. We report that spin-orbit interaction induces an opening of this fundamental gap of about 0.06 eV, which is smaller than the gap observed in experiment. To see the effects of electron-electron interaction on this fundamental gap, we calculate the quasiparticle electronic band structure within the GW approximation.

1. Introduction

Molybdenum disulfide (MoS₂) in its bulk form consists of layers of single-layer MoS₂ held together by weak van der Waals interaction. There exists three different stacking orders of these layers with trigonal prismatic and octahedral coordination of the Mo atom [1]. The aforementioned polytypes are 3R (three layers per repeated unit having rhombohedral symmetry), 2H (two layers per repeated unit having hexagonal symmetry), and 1T (one layer per repeated unit having trigonal symmetry) structures. 2H structure is more stable in nature, while 3R can transform to 2H upon heating [2]. Since the interaction between adjacent layers is weak while the interaction within the layers is strong, single-layer MoS₂ can be isolated from the bulk by means of mechanical exfoliation.

1H-MoS₂ is considered as the most stable single-layer MoS₂. Another structure in its single-layer is 1T, which can be achieved by annealing treatment of 1H on Au substrate [3]. However, it has been reported that 1T structure is not stable and immediately relaxes to a structure characterized by the formation of Mo-Mo zigzag chains. This new structure is called distorted 1T’, and is depicted in Figure 1. The authors in Ref. [4, 5] proposed that a spontaneous structural distortion of 1T to 1T’ structure leads to a band inversion in the band structure.

Recent experimental study demonstrated a 1H to 1T’ transition of MoS₂ on Au substrate upon annealing [5]. The authors concluded that the observed mid-infrared peak in the absorption spectrum around 0.5 eV corresponds to the inverted gap of the 1T’ structure since the peak only appears in MoS₂/Au, and not in MoS₂/Al₂O₃. However, theoretical calculation on the
Figure 1. Side and top views of single-layer 1T’-MoS$_2$, with atom S in yellow and atom Mo in gray.

absorption spectrum of 1T’-MoS$_2$ has not been reported so far, to the best of our knowledge. Therefore, it is important to calculate the absorption spectrum of this structure to clarify the findings reported in Ref. [3] and understand its underlying physics.

The main ingredient in the calculation of excited state properties such as the absorption spectrum is the reference ground state properties such as electronic band structure. In the present work, we perform electronic band structure calculation within density functional theory (DFT) in the local density approximation (LDA) and the absorption spectrum in the random phase approximation (RPA). Since DFT often underestimates the band gap of many semiconductors, a more reliable approach based on many-body perturbation theory in the GW approximation is applied to correctly capture the correlation effects arising among electrons. Spin-orbit coupling is included in the calculation and is shown to be important and responsible in the opening of the gap in 1T’-MoS$_2$. Furthermore, we demonstrate the importance of the choice of k-point sampling in the calculation of electronic band structure.

2. Methods and Computational Details
In this paper, quantities related to electronic ground state are calculated within density functional theory (DFT) in the local density approximation. The electronic ground state is represented by the solutions of the Kohn-Sham (KS) equation

$$\left[ -\nabla^2 + v_n(r) + v_H(r) + v_{xc}(r) \right] \phi^K_S(r) = \epsilon^K_S \phi^K_S(r),$$

which are calculated in the Quantum ESPRESSO package [6]. $\phi^K_S(r)$ and $\epsilon^K_S$ appearing in Eq. 1 are the Kohn-Sham wavefunctions and the corresponding energy eigenvalues, respectively. The wavefunction is expanded in a plane-wave basis set in which a large number of plane waves have to be included in the calculation to minimize the total energy and to describe the system correctly. To lower the computational cost, the number of plane waves is limited by introducing a cutoff energy corresponding to the number of plane waves used in the calculation. The cutoff energy of 60Ry applied in this work is sufficient to converge the total energy of the system. On the left hand side of Eq. 1, we have kinetic energy operator $-\nabla^2$ of an electron, external Coulomb potential $v_n(r)$ due to nuclei, mean-field Hartree potential $v_H(r)$ due to electron density, and exchange-correlation energy $v_{xc}(r)$ to account for all many-body effects felt by an electron. Using a plane-wave basis set for the wavefunction expansion, $v_n(r)$ often leads to a computational problem when dealing with core-electron states. The peak of such states are very sharp in the limit of $r = 0$, such that one requires a very large cutoff energy. For this reason, we use the optimized norm-conserving Vanderbilt and fully relativistic
pseudopotentials \[8\] to describe the core electrons and calculate its spin-orbit interaction. The structure of 1T'-MoS\(_2\) containing Mo-Mo clustering is simulated by using (2 \times 1) supercell (see Figure 1). The positions of the ions are relaxed until the Hellmann-Feynman forces acting on each ions are less than 10\(^{-6}\) eV/\(\text{Å}\). Furthermore, to simulate a single-layer of 1T'-MoS\(_2\), a vacuum space of more than 20\(\text{Å}\) is added in the direction normal to the two-dimensional plane.

DFT offers a powerful method for calculating the ground-state properties of a system of interacting electrons. However, apart from its well-established formulation, it remains a big challenge to use such an approach to capture effects arising from strong correlations among the electrons correctly. As a consequence of this, DFT fails to describe the correct band gap of semiconductors. A successful and more accurate approximation is based on many-body perturbation theory (MBPT). The idea is that the long-ranged Coulomb forces could screen individual electrons with surrounding cloud of the other electrons. This requires us to define an electron plus its screening cloud as a quasiparticle.

The quasiparticle energies \(E_{n\mathbf{k}}^{QP}\) and their wavefunctions \(\psi_{n\mathbf{k}}\) can be obtained by solving the following Schrödinger-like equation

\[
-\frac{\nabla^2}{2m} + v_n(r) + v_H(r) \psi_{n\mathbf{k}}(r) + \int \Sigma(\mathbf{r}, \mathbf{r}', E_{n\mathbf{k}}^{QP}) \psi_{n\mathbf{k}}(\mathbf{r}) d\mathbf{r}' = E_{n\mathbf{k}}^{QP} \psi_{n\mathbf{k}}(\mathbf{r}).
\]

Eq. 2 looks very similar to Eq. 1, except now we have non-local and energy dependent self-energy \(\Sigma(\mathbf{r}, \mathbf{r}', E_{n\mathbf{k}}^{QP})\). In 1965, Lars Hedin \[9\] described a way to calculate self-energy, in which the form of the self-energy gives the approximation the name \(GW\). In this approximation, the self-energy is the product of the single-particle Green’s function \(G\) and the screened interaction \(W\).

The calculation of self-energy in the \(GW\) approximation is carried out by using Yambo code \[10\]. In this code, the self-energy is separated into two parts, the exchange part \[10\]

\[
\Sigma^x_{n\mathbf{k}} = -\sum_m \int_{BZ} \frac{d\mathbf{q}}{(2\pi)^3} \sum_G v(\mathbf{q} + \mathbf{G}) |\rho_{nm}(\mathbf{k}, \mathbf{q}, \mathbf{G})|^2 f_{m(\mathbf{k}-\mathbf{q})},
\]

and the correlation part \[10\]

\[
\Sigma^c_{n\mathbf{k}}(\omega) = i \sum_m \int_{BZ} \frac{d\mathbf{q}}{(2\pi)^3} \sum_{G,G'} \rho_{nm}(\mathbf{k}, \mathbf{q}, \mathbf{G}) \rho^*_{nm}(\mathbf{k}, \mathbf{q}, \mathbf{G}') f_{m(\mathbf{k}-\mathbf{q})} \times \int d\omega' G^0_{m(\mathbf{k}-\mathbf{q})}(\omega - \omega') \epsilon^{-1}_{G,G'}(\mathbf{q}, \omega'),
\]

where \(v(\mathbf{q} + \mathbf{G}) = 4\pi/|\mathbf{q} + \mathbf{G}|^2\) is the bare Coulomb potential in the reciprocal space, \(\rho_{nm}(\mathbf{k}, \mathbf{q}, \mathbf{G}) = (\mathbf{n}|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|\mathbf{m} - \mathbf{q})\) is the oscillator matrix, \(f_{m(\mathbf{k}-\mathbf{q})}\) is the occupation factor, \(G^0_{m(\mathbf{k}-\mathbf{q})}(\omega - \omega')\) is the bare Green’s function, and \(\epsilon^{-1}_{G,G'}(\mathbf{q}, \omega')\) is the inverse dielectric matrix.

In the two expressions above, we have a summation over bands \(m\), an integral over \(\mathbf{k}\)-points in the first Brillouin zone (BZ), and a sum over the reciprocal vectors \(\mathbf{G}\). The summation over bands extends over all empty states, which is in principle infinity. In this work, we limit the number of states to 100 bands and use the method developed by Ref.\[11\] to speed up the convergence of \(GW\) calculation using only few empty bands. Furthermore, Monte Carlo integration method is used to avoid slow convergence due to the divergence at small momentum transfer \(\mathbf{q}\) of Coulomb potential in two-dimensional system \[10\].
3. Results and Discussion

In Figure 2, we show the band structure of 1T’-MoS$_2$ obtained by varying k-point grids. To this end, we use $n \times n$ Γ-centered Monkhorst-Pack [12] k-point grids as the Brillouin zone integration, where $n = 12, 18, 24, 30, 32, \text{ and } 36$. The band structure displays a band inversion at high symmetry point Γ with an inverted gap of $2\delta = 0.5$ eV. The value of this inverted gap is quantitatively in a good agreement with [3]. The band inversion already reveals without including spin-orbit interaction and quasiparticle corrections in the calculation.

In addition to the inverted gap, we also find a much smaller gap, called fundamental gap, at k-point between Y and Γ symmetry lines. Since this gap occurs at a non-high-symmetry point of the Brillouin zone, the choice of k-point sampling is crucial to understand the underlying physics of this 1T’ structure. As can be seen from the inset of Figure 2, the highest valence band and the lowest conduction band are overlapping for $n = 12$. This overlapping is reduced for $n = 24$ and further reduced for $n = 36$. On the other hand, we observe a gap for $n = 18$. By increasing the density of k-point sampling, this gap decreases. From this contrary behavior between $n = 12, 24, 36$ and $n = 18, 30, 32$, we believe that the two bands will touch each other for a very large $n$. This behavior is already observed for $n = 24$ and $n = 36$, suggesting that the k-point corresponding to transition at the fundamental gap is already included for k-point sampling of $24 \times 24$ and $36 \times 36$. In all calculations described above, we neglect spin-orbit coupling. It implies that the highest valence band and the lowest conduction band touch each other without spin-orbit coupling. Taking into account spin-orbit coupling in the calculation leads to an opening of fundamental gap of $E_g = 0.06$ eV, as shown in Figure 3.

Calculated band structure of 1T'-MoS$_2$ with and without GW correction is shown in Figure 4. The dashed lines represent the calculated band structure at DFT level in the local density approximation (LDA), while the colored lines represent $G_0W_0$ corrected band sturcture. We show that GW calculation leads to an opening of fundamental gap of $E_g = 0.1$ eV. This value is also consistent with the value observed in experiment [3]. However, as can be seen from the figure, the inverted gap is now reduced. Interestingly, the value of the inverted gap with and without GW correction does not correspond to any peaks in the absorption spectrum as
shown in Figure 5. Since the system is anisotropic, we calculate the absorption spectrum by varying the light polarization in the direction parallel to the two-dimensional plane, as displayed in the inset. We see that the spectra exhibit the same lineshape in all the directions of light polarization with different intensity of the low-energy peak at $\sim 0.1$. In the main panel, the spectrum is dominated by a sharp peak at $\sim 0.06$ eV and $\sim 0.1$ eV calculated on top of the LDA and $G_0W_0$ calculated ground states, respectively. The spectrum calculated on top of $G_0W_0$ calculated ground state is blueshifted as compared to that calculated on top of LDA calculated ground state, in accordance with the opening of the fundamental gap. It implies that this peak corresponds to transition at the fundamental gap. However, our calculated absorption spectra cannot accurately reproduce the structure observed in experiment. We believe that electron-phonon and electron-hole interactions have an important role in this regard and have to be included in the calculation to account for indirect transitions and excitonic effects, respectively.

![Figure 4](image1.png)

**Figure 4.** LDA (dashed black curves) and $G_0W_0$ (solid colored curves) electronic band structure of 1T'-MoS$_2$.

![Figure 5](image2.png)

**Figure 5.** Main panel: absorption spectra of 1T'-MoS$_2$ calculated using random phase approximation (RPA) with (red) and without (black) $GW$ correction; inset: absorption spectra with $GW$ correction calculated for light polarized in the $x$, $y$, and $xy$ directions.

### 4. Conclusion

In conclusion, we have calculated the electronic band structure in the LDA and $GW$ approximations taking into account spin-orbit interaction. At the LDA level without considering spin-orbit interaction, we demonstrate that the choice of $k$-point sampling is crucial in order to draw correct interpretations of the system in its ground state. The band structure displays a band inversion which already reveals at the LDA level neglecting spin-orbit interaction. Spin-orbit coupling, together with $GW$ quasiparticle correction, is responsible for the opening of the fundamental gap of $E_g = 0.1$ eV, which is qualitatively in a good agreement with the value observed in experiment. Our calculated absorption spectrum in the RPA taking only electron-electron interaction into account shows a sharp peak at the value of the fundamental gap. We argue that, to correctly capture the experimentally observed absorption spectrum, one has to include electron-phonon and electron-hole interactions to account for indirect transitions and excitonic effects, respectively.
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