Electronic properties of hybrid monolayer-multilayer MoS$_2$ nanostructured materials

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Abstract. The remarkable, layer-dependent properties of molybdenum disulphide (MoS$_2$), such as an appropriately small and sizable bandgap or interplay between spin and the valley degrees of freedom, make it an attractive candidate for photodetectors, electrominescent devices, valleytronic devices, etc. Using nanostructuring to manipulate the size in lateral direction or number of layers of MoS$_2$, we are opening a new playground for exploring and tuning properties of such systems. Here, we theoretically study the electronic properties of nanostructured MoS$_2$ systems consisting of monolayer and multilayer MoS$_2$ regions. In our analysis we consider hybrid systems in which monolayer region is surrounded by multilayer region and vice versa. We show how energy spectra and localization of carriers are influenced by the size and shape of the regions in lateral direction, number of MoS$_2$ layers in the multilayer region, and the edge structure. Finally, we demonstrate how to control localization of carriers in these hybrid systems, which could make them appealing candidates for optoelectronic devices. Our findings are extracted from a tight-binding model that includes non-orthogonal sp$^3$d$^5$ orbitals, nearest-neighbor hopping matrix elements, and spin-orbit coupling.

1. Introduction
Molybdenum disulphide (MoS$_2$), a transition metal dichalcogenide semiconductor, is a layered material in which each layer consists of hexagonal plane of Mo atoms sandwiched between two hexagonal planes of S atoms [1, 2, 3]. Layers are bounded by weak van der Waals type interactions, enabling a relatively straightforward exfoliation into two-dimensional (2D) monolayers. Consequently, MoS$_2$ exhibits remarkable, layer-dependent features, which makes it a promising candidate for a range of applications [2, 3, 4, 5, 6].

For example, in the monolayer limit, MoS$_2$ has a 1.8 eV direct band gap, located at the corners of the Brillouin zone, strong spin-orbit splitting, which is caused by the high mass of Mo and S, lack of inversion symmetry and confinement of carriers in a 2D layer, and also exhibit inequivalent valleys in the electronic structure. This offers prospects for optoelectronic-device applications [3], spintronic devices [4], or valleytronics [4, 3, 2].

Bilayer and multilayer MoS$_2$ have indirect band gaps. Interestingly, in the case of bilayer, the band gap can be tuned by an electric field applied perpendicular to the bilayer [7]. Multilayer MoS$_2$ have found their application in field-effect transistors [8, 5], where high mobilities and robust current saturation in a large voltage window were reported [8].

Furthermore, there have been experimental and theoretical studies on MoS$_2$ nanostructured materials. Examples include, mono- and multi-layer triangular nanoplatelets with side length up to 3.4 nm [9, 10], nano-flakes [5], and mono- and multi-layer nanowire arrays [11]. Actually,
nanostructuring opens the whole new playground to engineer MoS\(_2\)-based systems with different size and shape in lateral direction and varying number of layers within the structure.

Here, we theoretically study the electronic properties of nanostructured MoS\(_2\) systems consisting of monolayer and multilayer MoS\(_2\) regions. In our analysis we consider hybrid systems in which monolayer region is surrounded by multilayer region and vice versa. Theoretical predictions of electronic properties in those systems can provide guidelines for further experimental studies and potential practical optoelectronic applications [2, 6], including their targeted design [12]. Given an immense progress in fabrication techniques of reduced dimensionality MoS\(_2\) nanostructures, it not unreasonable to expect experimental realization and characterization of basically any arbitrary-shaped nanostructured MoS\(_2\) materials.

![Figure 1](image-url)

**Figure 1.** (a) MoS\(_2\) structure, \(a\) and \(c\) are lattice parameters. Black lines depict the unit cell of bulk MoS\(_2\); (b) model of hybrid monolayer-multilayer MoS\(_2\) nanostructured materials. The structures are characterized by two regions, 1ML and a multilayer region, specified by their size and shape and number of layer in the case of multilayer region.

### 2. Method

Model of the atomic structure of pristine MoS\(_2\) is shown in Figure 1(a). The bulk compound has 2H-MoS\(_2\) structure with two MoS\(_2\) layers per unit cell. Fig. 1(b) depicts model hybrid monolayer-multilayer MoS\(_2\) nanostructured materials analyzed in this work.

To resolve electronic structure of these hybrid systems, we employ an, in-house developed, tight-binding (TB) model that includes non-orthogonal sp\(^3\)d\(^5\) orbitals and spin-orbit coupling [13, 14, 15, 16]. For intra-layer S-S, Mo-S, and Mo-Mo interactions we consider nearest-neighbor and for inter-layer S-S interactions the second nearest neighbor hopping and overlap matrix elements. The spin-orbit interaction is assumed to arise only from the coupling of intra-atomic states with nonzero angular momentum [17, 18]. For our calculations we use a set of 96 TB parameters proposed by Zahid *et al.* [19, 20], which were fitted to the band structure of monolayer (1ML), bilayer (2ML), and bulk MoS\(_2\) obtained from density functional theory. Our calculated band structures for 1ML and 2ML pristine MoS\(_2\) are given in the Appendix.

### 3. Results and Discussion

Figure 2 shows calculated electronic properties of periodic arrays of MoS\(_2\) nanostructured materials and holes. Fig. 2(a) shows the calculated total electronic density of states (DOS) for pristine monolayer MoS\(_2\) [top panel] and how it changes when we introduce periodic array of 2ML disks [middle panel], and periodic array of holes [bottom panel]. Calculated electronic structure for 1ML of MoS\(_2\) with a periodic array of 2ML disks and holes is given in Fig. 2(b), left and right panels, respectively.

We see that presence of periodic arrays of either disks or holes changes states in the band gap, making these hybrid systems metallic-like. Also, the periodic array of holes has more pronounced effect on DOS than the periodic array of 2ML disks.
Figure 2. Calculated DOS (a) and electronic structure (b) of periodic arrays of MoS$_2$ nanostructured materials and holes (see text). Note that the energy range shown in (b) is smaller than in (a). In our calculation we used 6×6 supercell size, where 5×5 part is mapped to geometry shown in Fig. 1.

Figure 3 shows the calculated DOS of hybrid monolayer-multilayer MoS$_2$ nanostructured isolated disks [shape shown in Fig. 1]. If the region 2 is identical to the region 1 [see Fig. 1(b)], disk becomes uniform 1ML or 2ML disk, with calculated DOS shown in Fig.3(a). Analysis of

Figure 3. (a) DOS of isolated MoS$_2$ 1ML (left) and 2ML thick nano disk; (b) Influence of bump and divot in the region 2 of the disk [Fig. 1(b)] on DOS of MoS$_2$ disk (see text); (c) Calculated DOS of nano disk, where the region 2 is hole, $d_1$, $d_2$, and $d_3$ are different sizes of the hole.
partial DOS (not shown here) reveals that edge structure of the disk is responsible for those DOS variations. These findings are also in the agreement with the conclusions of Ref. [10].

Next, if we introduce 2ML and 3ML bump on a 1ML disk, or 1ML divot on 2ML disk, we obtain DOS as shown in Fig. 3(b). Compared to pure nano disks, we notice small differences. Thus, for the analyzed systems, the electronic structure is modified by the confinement of the nano disk, but not significantly influenced by the variation of the thickness in the region 2 of the structure.

On the other hand, DOS is significantly altered by adopting the region 2 to be a hole, Fig. 1(b). We vary the size of the hole, changing it from $d_1$, order of $a$, via $d_2 \sim 4a$, to $d_3$, which is chosen to be as large as possible not to break to break the ring of MoS$_2$ atoms. We see that the presence of the hole significantly changes DOS. Simply, this is a direct consequence of making the edge states much more dominant compared to the case of the disk.

In the case of hybrid monolayer-multilayer MoS$_2$ nanostructured isolated disks considered here [Fig.3(b)], variation of number of layers in the region 2 does not significantly influence DOS. However, presence of the hole and variation of its size [Fig. 1(c)], is obviously reflected in DOS. Experimentally, it could be possible to trace these differences in DOS, e.g., via dark/bright pattern contrast in STM images.

4. Conclusions
We theoretically studied the electronic properties of periodic and isolated nanostructured MoS$_2$ systems consisting of monolayer, multilayer MoS$_2$ regions, and holes. We found that by introducing a periodic array of disks or holes we change the character of the system to metallic-like. We showed that presence of a hole and its size in the nano disk is directly reflected in DOS, whereas DOS of the hybrid monolayer-multilayer MoS$_2$ nanostructured isolated disks is not significantly influenced by the variation of number of layers. Theoretical predictions of electronic properties in those systems coupled with the immense progress in fabrication techniques of reduced dimensionality MoS$_2$ nanostructures could open pathways for discovery and optimization of MoS$_2$-based optoelectronic devices.

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Appendix
Fig. A1(a) depicts the hexagonal Brillouin zone with the labeled high-symmetry points. Fig. A1(b) shows calculated band structure of single monolayer (1ML) and bilayer (2ML) MoS$_2$. 1ML MoS$_2$ is a direct band gap material, with valence band maximum (VBM) and conduction band minimum (CBM) located at high-symmetry point $K$ and 2ML MoS$_2$ has an indirect band gap, with VBM at $\Gamma$ and CBM at $K$. 
Figure A1. (a) The hexagonal Brillouin zone with labeled high-symmetry points. Red lines indicate paths along which the band structure are calculated (path Γ-K-M-Γ); (b) Band structure of monolayer (1ML) and bilayer (2ML) as extracted from our tight-binding calculations. The red arrows point out the lowest energy transitions.

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