Electronic and Optical properties of monolayer transition metal dichalcogenides under field-effect doping

Peiliang Zhao,1,2 Jin Yu,2 M. Rösner,2 Mikhail I. Katsnelson,2 and Shengjun Yuan1,*

1 Key Laboratory of Artificial Micro- and Nano-structures of Ministry of Education and School of Physics and Technology, Wuhan University, Wuhan 430072, China
2 Institute for Molecules and Materials, Radboud University, Heyendaalseweg 135, 6525AJ Nijmegen, The Netherlands

Doping via electrostatic gating is a powerful and widely used technique to tune the electron densities in layered materials. The microscopic details of how these setups affect the layered material are, however, subtle and call for careful theoretical treatments. In fact, the external gates do not just increase the Fermi level in the system, but also generate external electric fields which affect the layered material as well. As a result, the electron densities within the system can redistribute and might thereby affect the electronic band structure in a non-trivial way. Theoretical descriptions via rigid shifts of the Fermi level can therefore be highly inaccurate. Using semiconducting monolayers of transition metal dichalcogenides (TMDs) as prototypical systems affected by electrostatic gating, we show that the electronic and optical properties change indeed dramatically when the gating geometry is properly taken into account. This effect is implemented by a self-consistent calculation of the Coulomb interaction between the charges in different sub-layers within the tight-binding approximation. Thereby we consider both, single- and double-sided gating. Our results show that, at low doping levels of $10^{13}$ cm$^{-2}$, the electronic bands of monolayer TMDs shift rigidly for both types of gating, and subsequently undergo a Lifshitz transition. When approaching the doping level of $10^{14}$ cm$^{-2}$, the band structure changes dramatically, especially in the case of single-sided gating where we find that monolayer MoS$_2$ and WS$_2$ become indirect gap semiconductors. The optical conductivities calculated within linear response theory also show clear signatures of these doping-induced band structure renormalizations. Our numerical results based on light-weighted tight-binding models indicate the importance of electronic screening in doped layered structures, and pave the way for further understanding gated super-lattice structures formed by multilayers with extended Moiré pattern.

I. INTRODUCTION

Semiconducting transition metal dichalcogenides (TMDs) monolayers (MX$_2$ with M=Mo, W and X=S, Se) are direct gap semiconductors with optical gaps in the visible and near-infrared spectral range$^{2-4}$. Due to a variety of electronic, optical$^{6-9}$ and valleytronics$^{10-11}$ properties, TMDs are expected to be utilized in various electronic and optoelectronic devices$^{4,7,12}$ such as field effect transistors$^{13-15}$, photodetectors$^{16-19}$, modulators$^{20,21}$ and electroluminescent devices$^{22,23}$. When stacked with other two-dimensional (2D) materials such as graphene or hexagonal boron nitride, the resulting heterostructures can show highly sensitive photodetection and gate-tunable persistent photoconductivity at room temperature$^{24-27}$. Upon electron-doping using ionic liquid gates a plethora of phases ranging from semimetallic, to metallic and superconducting regimes can be probed in TMDs and even charge and magnetic order can be induced$^{28-32}$. This field-effect induced doping can accumulate up to $10^{14}$ electrons per cm$^2$ in the layer, which can correspondingly affect all of these correlation effects.

Here, we explore the electronic and optical properties of TMDs under the influence of those external electric fields resulting from asymmetric one- and symmetric two-sided gates. Based on an accurate multi-orbital tight-binding model$^{33,34}$, we implement a method$^{35-37}$ to self-consistently calculate the induced charge (re)distribution within the different sub-layers of TMD monolayers. Our results show that, for low doping levels up to about $10^{13}$ cm$^{-2}$, the band structure close to the conduction band minimum remains basically unaffected and shifts downward as the doping level increases. Upon further increasing the doping level to about $10^{14}$ cm$^{-2}$, the lowest conduction and upmost valence bands change remarkably under one-side gating. In the cases of MoS$_2$ and WS$_2$ these changes can yield direct to indirect band gap transitions. In contrast to the asymmetric gating, the symmetric gating geometry with two gates hardly affects the band structures of all tested TMDs and just changes the Fermi level. Finally, we discuss the importance of the embedded screening effects of the self-consistent method applied here.

The paper is organized as following: In Sec.II the TMD tight-binding model is introduced together with a self-consistent calculation in the presence of one- or two-sided gates. In Sec.III and Sec.IV the electronic structure and optical spectroscopy of gated TMDs are studied in low and high doping regime, followed by a brief discussion and conclusion in Sec.V.
The TMD crystals in our simulations are monolayers in the 2H-phase, which are formed by a top (XT) and a bottom (XB) chalcogen sub-layer, and a transition metal middle-plane M. We model the undoped electronic band-structure utilizing a full-range tight-binding model consisting of five M d orbitals and three X p orbitals. The Hilbert space is defined by

$$\psi^{\dagger}_{R_i} = |\varphi^{\dagger}_{R_i,x} P_{R_i,y} P_{R_i,z}^\alpha \rangle,$$

$$d^\dagger_{R_i,x}, d^\dagger_{R_i,xy}, d^\dagger_{R_i,xz}, d^\dagger_{R_i,y}, d^\dagger_{R_i,zy},$$

where $$d_{R_i,\alpha}(p_{R_i,\alpha})$$ creates an electron in the orbital $$\alpha$$ of M(X) atom in the $$R_i$$-unit cell. Using this basis the tight-binding Hamiltonian is given by:

$$H_0 = \sum_k \phi_k \hat{H}_0, \phi_k,$$

where $$\phi_k$$ is the Fourier transform of $$\psi_{R_i}$$ in momentum space. The Hamiltonian $$\hat{H}_0$$ can be written as (we omit the index $$k$$ for simplicity from now on):

$$\hat{H}_0 = \begin{pmatrix} \hat{H}_{\hat{p}_x,p_x} & \hat{H}_{\hat{d},p_x} & \hat{H}_{\hat{p}_x,p_0} \\ \hat{H}_{\hat{d},p_x} & \hat{H}_{\hat{d},d} & \hat{H}_{\hat{d},p_0} \\ \hat{H}_{\hat{p}_x,p_0} & \hat{H}_{\hat{d},p_0} & \hat{H}_{\hat{p}_x,p_0} \end{pmatrix}.$$

All involved lattice parameters are given in Table I, where $$a$$ and $$c$$ are the in- and out-of-plane lattice constants, and $$d$$ is the sub-layer distance between the M and X planes. The tight-binding parametrization is taken from from Ref. 34.

Upon gating the TMD monolayer and applying an external electric field additional (excess) electrons will accumulate within the monolayer, as shown in Fig. 1. In detail, an asymmetric one-sided gate creates an uniform electric field $$E = ne/e\epsilon_0 A$$, where $$n = n_1 + n_2 + n_3$$ is the excess electron density, with $$n_1$$ ($$n_3$$) describing the excess electron density in the bottom (top) X-sublayer and $$n_2$$ the excess electron density on the middle M-sublayer. The induced excess electrons $$n_i$$ redistribute as a reaction to this external gate field and create in turn uniform electric fields $$E_i (i = 1,2)$$ between the sub-layers, where $$E_1 = (n_2 + n_3)e/\epsilon_0$$ and $$E_2 = n_3e/\epsilon_0$$. This effectively screens the external gate field.

In order to find the correct distribution of these excess electron densities $$n_i$$, we make use of the self-consistent approach from Refs. 35–37. Accordingly, $$n_i$$ create electrostatic potentials $$\Delta_i (i = 1,2,3)$$ in each sub-layer, which are given in the one-sided gating setup by

$$\Delta_1(n) = \alpha(n_2 + n_3),$$

$$\Delta_3(n) = -\alpha n_3,$$

where $$\alpha = -e^2d/\epsilon_0\kappa$$, $$n = (n_1, n_2, n_3)$$, $$\epsilon_0$$ is the vacuum permittivity and $$\kappa$$ is the dielectric constant of setup. In this paper, we choose SiO₂ to gate TMDs and set $$\kappa = (1.0 + \kappa[SiO₂])/2$$. In both one- or two-sided geometries, electrostatic potentials $$\Delta_2$$ in the M middle layer is regard as zero potential plane. The one-sided gating geometry thus introduces a sub-layer asymmetry. For the two-sided gating setup, positive charge carriers are introduced equally in the outmost X sub-layers, retaining the mirror symmetry with respect to the M-plane. As a result we find

$$\Delta_1(n) = \Delta_3(n) = \beta n_2,$$

with $$\beta = -e^2d/2\epsilon_0\kappa$$. The full Hamiltonian in the presence of the external electric field is thus given by

$$\hat{H}(n) = \hat{H}_0 + \begin{pmatrix} \Delta_1(n) & \cdots & \Delta_3(n) \end{pmatrix},$$

with 3×3 matrices $$\Delta_1(n)$$ and $$\Delta_3(n)$$. Using the resolved density of states (DOS)

$$\rho(\epsilon) = \frac{1}{2\pi} \sum_{n=0}^{10} \int_{-\infty}^{\infty} \delta[\epsilon - E_n(k)]dk,$$
and eigenfunction of $\hat{H}(n)$

$$\phi_k^\uparrow = \left| c_{k,p_x}^{T\dagger}, c_{k,p_y}^{T\dagger}, c_{k,d_x}^{T\dagger}, c_{k,d_y}^{T\dagger}, c_{k,d_{2\gamma}}^{T\dagger}, c_{k,d_{3\gamma}}^{T\dagger}, c_{k,p_x}^{B\dagger}, c_{k,p_y}^{B\dagger}, c_{k,p_z}^{B\dagger}\right|,$$

(9)

the sub-layer DOS naturally given by

$$\rho_1(\varepsilon) = \frac{1}{2\pi} \sum_{n=0}^{10} \int_{BZ} \delta[\varepsilon - E_n(k)] \left( |c_{k,p_x}^{B\dagger}|^2 + |c_{k,p_y}^{B\dagger}|^2 \right. \left. + |c_{k,p_z}^{B\dagger}|^2 \right) dk,$$

(10)

$$\rho_2(\varepsilon) = \frac{1}{2\pi} \sum_{n=0}^{10} \int_{BZ} \delta[\varepsilon - E_n(k)] \left( |c_{k,d_x}^{T\dagger}|^2 + |c_{k,d_y}^{T\dagger}|^2 \right. \left. + |c_{k,d_{2\gamma}}^{T\dagger}|^2 + |c_{k,d_{3\gamma}}^{T\dagger}|^2 \right) dk,$$

(11)

$$\rho_3(\varepsilon) = \frac{1}{2\pi} \sum_{n=0}^{10} \int_{BZ} \delta[\varepsilon - E_n(k)] \left( |c_{k,p_x}^{T\dagger}|^2 + |c_{k,p_y}^{T\dagger}|^2 \right. \left. + |c_{k,p_z}^{T\dagger}|^2 \right) dk.$$

(12)

We vary all $n_i$ until we find a self-consistent solution according to $n_i = \int_{0}^{\Delta E_F} \rho_i(\varepsilon) d\varepsilon$ with $\Delta E_F = E_F(n) - E_F(0)$ and $E_F(n)$ being the doping-dependent Fermi level.

III. ELECTRONIC BAND STRUCTURE

We start wit plotting the pristine (i.e. undoped) band structure of monolayer MoS$_2$ in Fig. 2, which shows the $K$ and $Q$ electron pockets of the valence band. Upon electron doping these pockets become successively occupied while they both shift in energy due to the doping-induced potentials $\Delta_i$. Since the latter are defined by the self-consistently calculated partial excess electron densities $n_i$ we start with analyzing them as a function of doping level $n_i$ as shown for MoS2 in the lower panel of Fig. 3 for both gating setups. The excess electrons are distributed unevenly between the sub-layers with the main contribution on the central Mo-layer and smaller contributions on the chalcogen atoms. Upon increasing the doping level $n_i$ electrons get further localized on the Mo layer. For the one-sided gating, the excess electron density on the first layer, which is closest to the gate, is slightly larger than those on the third layer. Due to the symmetric $\Delta_1 = \Delta_3$ in the two-sided gating geometry, $n_1$ and $n_3$ are also symmetrically distributed to the chalcogen sub-layers. For $n = 1.0 \times 10^{14}$ cm$^{-2}$ we find that about 72% of doping electrons are located on the Mo layer, while 15% and 12% are accumulated at the S layer.
we show the change in the rigid-shifts (i.e. without any screening). For all of these scenarios $E_F(n)$ naturally increases with electron doping $n$. The two gate geometries behave rather similar, with the only difference of a slightly reduced shift in the case of the two-sided gates. In contrast, the rigid-shift approximation strongly underestimates the shifts of the Fermi level due to missing renormalizations of the band structure. From the comparison to the rigid-shift scenario, we understand that the doping-induced band structure renormalizations are the strongest in the one-sided gating geometry. This effect is correspondingly slightly reduced the symmetric two-sided gating geometry, but still non-negligible. Next to these renormalization-induced effects, we clearly see a reduced enhancement of $\Delta E_F(n)$ for $n > 6 \times 10^{13} \text{cm}^{-2}$. We attribute this to the occupation of the $Q$ valleys, which slows down the Fermi level shift and induces a Lifshitz transition, which we will discuss in detail in the following.

To this end we analyze the band structures of MoS$2$, WS$2$, and WSe$2$ for different doping levels and both gating geometries in Fig. 4. Overall, all materials behave rather similar for the depicted “low” electron doping regimes ($n \leq 1 \times 10^{14} \text{cm}^{-2}$), in which mostly the $K$ valley gets occupied and doping-induced band structure renormalizations are rather small. From this we also see that the changes in the Fermi levels (as measured from the bottom of the $K$ valley) are rather large as long as just $K$ is occupied. As soon as $Q$ get occupied as well the shift in the Fermi level slow drastically down. Note that the $Q$ point is not a high symmetric point in BZ and its exact position depends on the electron density $n$ and charge distribution. Our analysis shows that the orbital character at the $Q$ point originates mainly from the hybridization of the chalcogen $p$ orbitals and transition metal $M d_{xy}$, $d_{x^2-y^2}$, and $d_{3z^2-r^2}$ orbitals, in contrast to $K$ where we mostly find $M d_{3z^2-r^2}$ character. Thus, as

for the one-sided gate. In the case of the two-sided gates, about 73% of the excess electrons are located at the Mo layer and about 13.5% part on S layer. This enhanced inhomogeneity in the layer-resolved charge distribution in TMD monoalayers was also reported in Ref. 38.

In the upper panel of Fig. 3 we show the change in the Fermi level $\Delta E_F(n)$ as a function of gate-induced doping for MoS$2$ for both gating geometries and for simple rigid-shifts (i.e. without any screening). For all of these scenarios $E_F(n)$ naturally increases with electron doping $n$. The two gate geometries behave rather similar, with the only difference of a slightly reduced shift in the case of the two-sided gates. In contrast, the rigid-shift approximation strongly underestimates the shifts of the Fermi level due to missing renormalizations of the band structure. From the comparison to the rigid-shift scenario, we understand that the doping-induced band structure renormalizations are the strongest in the one-sided gating geometry. This effect is correspondingly slightly reduced the symmetric two-sided gating geometry, but still non-negligible. Next to these renormalization-induced effects, we clearly see a reduced enhancement of $\Delta E_F(n)$ for $n > 6 \times 10^{13} \text{cm}^{-2}$. We attribute this to the occupation of the $Q$ valleys, which slows down the Fermi level shift and induces a Lifshitz transition, which we will discuss in detail in the following.

To this end we analyze the band structures of MoS$2$, WS$2$, and WSe$2$ for different doping levels and both gating geometries in Fig. 4. Overall, all materials behave rather similar for the depicted “low” electron doping regimes ($n \leq 1 \times 10^{14} \text{cm}^{-2}$), in which mostly the $K$ valley gets occupied and doping-induced band structure renormalizations are rather small. From this we also see that the changes in the Fermi levels (as measured from the bottom of the $K$ valley) are rather large as long as just $K$ is occupied. As soon as $Q$ get occupied as well the shift in the Fermi level slow drastically down. Note that the $Q$ point is not a high symmetric point in BZ and its exact position depends on the electron density $n$ and charge distribution. Our analysis shows that the orbital character at the $Q$ point originates mainly from the hybridization of the chalcogen $p$ orbitals and transition metal $M d_{xy}$, $d_{x^2-y^2}$, and $d_{3z^2-r^2}$ orbitals, in contrast to $K$ where we mostly find $M d_{3z^2-r^2}$ character. Thus, as
soon as the six \( Q \) valleys get occupied the doping-induced band structure renormalization via \( \Delta_1 \) and \( \Delta_3 \) become more important, so that the resulting renormalization effects are stronger.

As the \( Q \) valleys starts to get populated, TMDs undergo a Lifshitz transition that reconstructs the Fermi surface\(^{39\text{-}43} \). Six new Fermi pockets centered around \( Q/Q' \) appear in the BZ and the Fermi surface topology changes with electron doping. In contrast to MoS\(_2\) and WS\(_2\), the difference between the band structures and their doping dependence in the one-sided and two-sided gating geometries for WSe\(_2\) is not negligible. The critical electron doping level that occupies the \( Q/Q' \) valleys is clearly dependent on the gating setup in WSe\(_2\). With the one-sided gate, the Lifshitz transition happens at \( n = 9.0 \times 10^{13} \) \( \text{cm}^{-2} \), while for the two-sided gates, the corresponding electron doping level is \( n = 8.0 \times 10^{13} \) \( \text{cm}^{-2} \).

In Fig. 5 we show the corresponding band structures for high doping densities. Here, in the one-sided gate geometry strong bandstructure renormalizations are observed, which cannot be described by simple rigid-shifts of the Fermi level. For MoS\(_2\) and WS\(_2\) [Fig. 5 (a) and (b)] these renormalizations can shift the conduction band edge from \( K \) to \( Q \), resulting in a direct to indirect band-gap transition consistent with previous DFT and numerical results\(^{38,44} \). For WSe\(_2\), much higher electron doping densities are needed to realize such a transition. Another important characteristic in high-doping regime is the renormalization of the \( K \) valley as a function of \( n \). In contrast to the low-doping regime, the pocket around the \( K \) point shifts upward when the doping density increases. In the low-doping regime, the \( K \) pocket shifts slowly down with increasing \( n \). Due to the symmetric \( \Delta_1 = \Delta_3 \) in the double-sided gate geometry, inter-valley renormalizations in the high-doping regime are strongly reduced in comparison to the single-sided gate. In this case, the shifts of the conduction band are however enhanced, as shown in Fig. 5 (d) and (f). The \( K \) valley is shifted by more than 600 meV (500 meV) for WSe\(_2\) (WS\(_2\)). In addition, the \( Q \) valley is moving towards \( K \) valley with increasing \( n \), as also observed in low-doping regime. Through high electron doping we can thus tune the Fermi surface topology and the relative alignment between the

![Band structures for electron-doped TMDs in high doping regime](image-url)

FIG. 5. Band structures for electron-doped TMDs in high doping regime \( 2.0 \times 10^{14} \) \( \text{cm}^{-2} \leq n \leq 4.0 \times 10^{14} \) \( \text{cm}^{-2} \). The figures (a) (b) (c) are for one-side gate, (d) (e) (f) show the two-sides gate case. Blue dotted lines are for pristine TMDs, red dash-dotted lines are for TMDs with electron doping \( n = 2.0 \times 10^{14} \) \( \text{cm}^{-2} \), purple dotted lines and green solid lines correspond to \( n = 3.0 \times 10^{14} \) \( \text{cm}^{-2} \) and \( n = 4.0 \times 10^{14} \) \( \text{cm}^{-2} \) cases.
theory, which we calculate by using the Kubo formula to the optical conductivity within the linear response

\[ \sigma(\omega) = \lim_{\epsilon \to \infty} \frac{e^{-\beta \omega} - 1}{\omega A} \int_0^\infty e^{-\epsilon t} \sin \omega t \times 2 \text{Im} \langle \varphi | f(H) J(t) | 1 - f(H) \rangle J|\varphi \rangle \, dt. \]

(13)

Here, \( \beta = 1/k_B T \) is the inverse temperature, \( A \) is the sample area, \( f(H) = 1/[e^{\beta(H-\mu_F)} + 1] \) is the Fermi-Dirac distribution operator and \( \mu_F \) is the chemical potential. In order to alleviate the effects of the finite time \( (\tau) \) in the numerical time integration, we adopt a Gaussian window of \( 10^{-\epsilon(t/\tau)^2} \) with \( \epsilon = 2 \) in Eq. (13).

In Fig. 6 we show the resulting optical conductivities for all TMDs for plain rigid-shifts (thus neglecting any renormalization and screening effects) and with applying the gate-induced doping. We find in all calculations ad-
ditional features around $\omega \approx 1$ eV due to finite electron doping within the former optical gap. These additional signals get wider and shift to smaller energies upon increasing the doping density $n$. Overall, these features behave rather similar in the three doping scenarios, with two exception for MoS2 and WS2: in the single-sided gate geometry the doping-induced signals show sharp peaks for $n = 3.0 \times 10^{14}$ cm$^{-2}$ (MoS2) and $n = 4.0 \times 10^{14}$ cm$^{-2}$ (WS2), where the direct- to indirect-gap transitions occur. It is remarkable, how similar these doping-induced optical features behave in the rigid-shift and double-sided gating situations, having in mind how strongly the band structure in the latter case is renormalized.

The optical signals from about $\omega = 2$ eV to $\omega = 4$ eV in the rigid-shift scenario do not change drastically upon increasing doping. Here, the only difference is the increasing (and smoothing) of the optical gap due to the increasing Fermi level within the conduction bands (these features arise due to excitations from valence to unoccupied conduction states). If we account for band structure renormalizations within the single- and double-sided gate setups, the sharp features in this frequency range start to shift. These are associated with optical transitions between van Hove singularities at $M$ and $Q$ in the valence band and empty states in the conduction band, which exhibit blue shifts with increasing doping density. Band structure renormalizations should thus be visible in optical spectra. We, however, also see a slightly increasing optical gap in the gate-induced doping scenarios, which are resulting from doping-induced increasing band gaps in our calculations.

V. DISCUSSION AND CONCLUSIONS

We numerically studied the electronic and optical properties of electron-doped TMD monolayers by gating, considering single- and double-sided gate geometries. The redistribution of the induced excess electron densities within the sub-layers of the TMD monolayers due to the applied gate field is self-consistently accounted for within a light-weighted tight-binding approach. Thereby static screening of the external gate field is intrinsically captured. The latter yield band structure renormalizations, prominently observed as relative shifts between the $K$ and $Q$ valleys in the conduction band. These renormalizations can have important consequences: On one hand, they define the critical doping density corresponding to a Lifshitz transition, which drastically changes the Fermi surface topology by occupying the $Q$ pockets. On the other hand, these renormalization effects can be strong enough to induce a direct to indirect band-gap transition by shifting the $Q$ valley below the $K$ valley. Interestingly, the different TMDs exhibit opposite sensitivities at different doping levels. While in the low-doping regime the WSe2 band structure renormalizations are most sensitive to the doping (in comparison to WS2 and MoS2), the MoS2 band structure is most sensitive to electron doping in the high-density regime. These results are in-line with similar calculations based on full ab initio calculations applying density functional theory and show that the commonly used rigid shift of the Fermi level in doped layered structures might miss important effects. This tight-binding based approach can be straightforwardly generalized to structures with large supercells, such as twisted multilayers and their heterostructures, or Moiré patterns. These generally contain a large number of atoms which can easily exceed the computational limits of density functional calculations.

Regarding the consequences of the band structure renormalizations to TMDs, the possibility to perfectly align the $K$ and $Q$ valleys in MoS2 and WS2 can be useful to design valleytronic devices, as they might show an optimal performance when two or more valleys are available at similar energies but at different positions in momentum space. Considering a fact that the electron-phonon interaction in electron-doped TMDs depends strongly on which valleys of the conduction band are occupied, as the orbital character of electronic states differ substantially in different valleys, our results may help to explain the superconducting dome in gated TMDs, as well as details of charge-density ordering.

Regarding optical properties, we clearly showed the existence of additional doping-induced features in the optical conductivity of TMD monolayers. While these doping-induced features are similarly affected by the doping level in both, rigid-shift and gate-induced, scenarios, optical features at energies larger than the electronic band gap, certainly display changes induced by band-structure renormalizations, which are not present in the rigid-shift-like doping. Thus, optical probes can help to monitor both, the doping level and the correspondingly induced band renormalizations, rendering them a powerful tool to characterize doping-induced effects.

Here we, however, also see a clear shortcoming of our approach: The optical gaps increase upon doping, which result from increasing electronic band gaps in our calculations. This contradicts the decreasing trends seen in GW-like calculations for increasing Fermi levels, which are experimentally verified upon optical doping. While these GW-like calculations take the full long-range Coulomb interaction and the internal screening of these interactions into account, our calculations describe local effects only. Thus, our calculations can be seen as a mean-filed treatment with local Coulomb interactions only, whereby the latter are successively reduced (screened) upon increasing doping concentration. And indeed, analogous LDA+U calculations also show an increasing electronic band gap upon decreasing (screening) U. As discussed in Ref. 51, the band gap in semiconducting TMDs mostly results from hybridization effects between the transition metal d orbitals. These hybridization effects are enhanced by long-range Coulomb interactions, which explains the increased band gap in GW calculations for TMD monolayers in contrast to plain DFT.
calculations\textsuperscript{32}. Thus, upon increasing screening due to increased Fermi levels the long-range Coulomb interaction is decreased, which decreases the d-orbital hybridization, which in turn must reduce the electronic band gap. Nevertheless, the local gate-field induced changes described here must be considered as well, which are so far missing in standard GW calculations. Thus, in order to achieve a full quantitative description of gate-induced doping effects in layered materials, GW-like calculations are needed which take the external gate-field into account.

\textbf{ACKNOWLEDGMENTS}

We acknowledge helpful discussions with J. Silva-Guillé, H. Zhong and G. Yu. This work was supported by the National Key R&D Program of China (Grant No. 2018FYA0305800) and M.I.K. thanks financial support from JTC-FLAGERAProject GRANSORT. Numerical calculations presented in this paper were performed on the Supercomputing Center of Wuhan University.
Nano Letters 18, 4821 (2018).
33 E. Cappelluti, R. Roldán, J. A. Silva-Guillén, P. Ordejón, and F. Guinea, Physical Review B 88, 075409 (2013).
34 J. Silva-Guillén, P. San-Jose, and R. Roldán, Applied Sciences 6, 284 (2016).
35 E. McCann, Physical Review B 74, 161403 (2006).
36 E. V. Castro, K. S. Novoselov, S. V. Morozov, N. M. R. Peres, J. M. B. L. dos Santos, J. Nilsson, F. Guinea, A. K. Geim, and A. H. C. Neto, Physical Review Letters 99, 216802 (2007).
37 A. A. Avetisyan, B. Partoens, and F. M. Peeters, Physical Review B 79, 035421 (2009).
38 T. Brumme, M. Calandra, and F. Mauri, Physical Review B 91, 155436 (2015), arXiv: 1501.07223.
39 Y. P. Shkolnikov, E. P. De Poortere, E. Tutuc, and M. Shayegan, Physical Review Letters 89, 226805 (2002).
40 A. Rycerz, J. Tworzydo, and C. W. J. Beenakker, Nature Physics 3, 172 (2007).
41 D. Xiao, W. Yao, and Q. Niu, Physical Review Letters 99, 236809 (2007).
42 C. Liu, T. Kondo, R. M. Fernandes, A. D. Palczewski, E. D. Mun, N. Ni, A. N. Thaler, A. Bostwick, E. Rotenberg, J. Schmalian, S. L. Budko, P. C. Canfield, and A. Kaminski, Nature Physics 6, 419 (2010).
43 G. Schnhoff, M. Rsner, R. E. Groenewald, S. Haas, and T. O. Wehling, Physical Review B 94, 134504 (2016).
44 D. Erben, A. Steinhoff, C. Gies, G. Schnhoff, T. O. Wehling, and F. Jahnke, Physical Review B 98, 035434 (2018).
45 A. Ishihara, Statistical Physics (Academic Press, New York, 1971).
46 S. Yuan, H. De Raedt, and M. I. Katsnelson, Phys. Rev. B 82, 115448 (2010).
47 Y. Ge and A. Y. Liu, Physical Review B 87, 241408 (2013).
48 J. Lu, O. Zheliuk, Q. Chen, I. Leermakers, N. E. Hussey, U. Zeitler, and J. Ye, PNAS 115, 3551 (2018).
49 A. Steinhoff, M. Rsner, F. Jahnke, T. O. Wehling, and C. Gies, Nano Letters 14, 3743 (2014), pMID: 24956358.
50 E. J. Sie, A. J. Frenzel, Y.-H. Lee, J. Kong, and N. Gedik, Phys. Rev. B 92, 125417 (2015).
51 M. Rsner, C. Steinke, M. Lorke, C. Gies, F. Jahnke, and T. O. Wehling, Nano Letters 16, 2322 (2016), pMID: 26018626.
52 S. Haastrup, M. Strange, M. Pandey, T. Deilmann, P. S. Schmidt, N. F. Hinsche, M. N. Gjerding, D. Torelli, P. M. Larsen, A. C. Riis-Jensen, J. Gath, K. W. Jacobsen, J. J. Mortensen, T. Olsen, and K. S. Thygesen, 2D Materials 5, 042002 (2018).