First-principle theory of field-effect doping in transition-metal dichalcogenides: structural properties, electronic structure, Hall coefficient, and electrical conductivity

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We investigate how field-effect doping affects the structural properties, the electronic structure and the Hall coefficient of few-layers transition metal dichalcogenides by using density-functional theory. We consider mono-, bi-, and trilayers of MoS\(_2\), MoSe\(_2\), MoTe\(_2\), WS\(_2\), and WSe\(_2\) and provide a full database of electronic structures and Hall coefficients for hole and electron doping. We find that, for both electron and hole doping, the electronic structure cannot be described by a rigid band shift and that it is important to relax the structure under the asymmetric electric field. For multilayer dichalcogenides, in the range of hole or electron doping relevant for ionic-liquid based field-effect transistor, we demonstrate that the electronic structure is very different from the monolayer case and that it is incompatible with both the rigid doping and the uniform-background doping approach. Furthermore, for hole doping the width of the conducting channel decreases from three to one layer as the induced charge increases from \(+10^{13}\) cm\(^{-2}\) to \(+3.5 \cdot 10^{14}\) cm\(^{-2}\). On the contrary, for small electron doping of \(\approx -10^{13}\) cm\(^{-2}\) the width varies between one and three layers in different dichalcogenides. Increasing the number of electrons leads however also to a reduced width of just one layer. Interestingly, the number of occupied bands at each given \(\mathbf{k}\) point is almost uncorrelated with the thickness of the doping-charge distribution. Finally, we calculate within the constant-relaxation-time approximation the electrical conductivity and the inverse Hall coefficient. We demonstrate that in some cases the charge determined by Hall-effect measurements can deviate from the real charge by up to 50%. The error is even larger for hole-doped MoTe\(_2\), where the Hall charge has even the wrong polarity at low temperature. We thus provide the mapping between the doping charge and the Hall coefficient. In the appendix we present more than 250 band structures for all doping levels of the transition-metal dichalcogenides considered within this work.

I. INTRODUCTION

Since the rise of graphene\(^1\) and the discovery of topological insulators\(^2\) a lot of interesting physics has been found in systems with reduced dimensions. Other two-dimensional (2D) material, such as monolayers or few-layer systems (nanolayers) of transition-metal dichalcogenides (TMDs) are gaining importance because of their intrinsic band gap. TMDs are MX\(_2\)-type compounds where M is a transition metal (e.g., M = Mo, W) and X represents a chalcogen (S, Se, Te). These materials form layered structures in which the different X–M–X layers are held together by weak van der Waals forces. Thus, similar to graphene, one can easily extract single or few layers from the bulk compound using the mechanical-exfoliation or other experimental techniques.

Doping these nanolayers with field-effect transistors (FETs) is particularly appealing\(^3\) as it allows to explore the semiconducting, metallic, superconducting and charge-density wave regimes in reduced dimensionality. Furthermore, the TMDs are promising materials to realize valleytronics, i.e., the usage of the valley index of carriers to process information\(^4\). Relevant for ionic-liquid based FETs, by assuming that only the topmost layer is doped uniformly. However, it is unclear to what extent the doping of thick flakes can be modeled in this approximation as the thickness of the conductive channel is not experimentally accessible.

A second crucial issue is the determination of the doping charge. Usually the charge is determined via Hall-effect measurements. However, the interpretation of Hall experiments assumes a 2D electron-gas model, most likely valid only in the low doping regime. In TMDs, due to the multivalley electronic structure, this assumption is highly questionable.

In this paper we solve these issues and provide a thoroughly study of structural, electronic and transport properties and of their changes under field-effect doping for TMDs. We use our recently developed first-principles theoretical approach to model doping in field-effect devices\(^5\). The method allows for calculation of the electronic structure as well as complete structural relaxation in field-effect configuration using density-functional theory (DFT). We apply our approach to the H polytype of MoS\(_2\), MoSe\(_2\), MoTe\(_2\), WS\(_2\), and WSe\(_2\).

The paper is organized as follows: In section II we summarize the parameters and methods used within the paper and the relaxed geometries of the bulk TMDs. Then we will first show the results for the undoped mono-, bi-, and trilayer systems (section III A). After a brief discussion on the quantum capacitance (III B), we will investigate the changes of the geometry and the electronic...
structure of the different TMDs in section II C and II D respectively. Finally, we will focus on how the doping-charge concentration can be determined experimentally by Hall-effect measurements. We will show in section II E that the results of such a measurement cannot be interpreted within a 2D electron-gas model but that the specific band structure of the TMDs and its changes in a field-effect setup need to be taken into account. In section II F we will furthermore investigate the density of states (DOS) at the Fermi energy and the electrical conductivity as function of doping. In the end, we will summarize our results and draw some final conclusion in section IV. In the appendix we provide a full database of electronic structures for all doping levels considered in this work (in total more than 250 calculations, Figs. 27–62) and Hall coefficients (Figs. 63–65) of mono-, bi-, and trilayer dichalcogenides as a function of doping.

II. COMPUTATIONAL DETAILS

All calculations were performed within the framework of DFT using the Quantum ESPRESSO package\(^\text{28}\) which uses a plane-wave basis set to describe the valence-electron wave function and charge density. We employed full-relativistic, projector augmented wave potential\(^\text{26}\) and the Perdew-Burke-Ernzerhof functional (PBE) for the exchange-correlation energy. We furthermore included dispersion corrections\(^\text{26}\) (D2).

Using the experimental lattice parameters of the bulk structures\(^\text{28}\) as starting geometry, we minimized the total energy as function of the lattice parameters until it changed by less then 2 meV. For the molybdenum containing dichalcogenides we used a cutoff of 50 Ry and 410 Ry (1 Ry \(\approx\) 13.6 eV) for the wave functions and the charge density, respectively, while for the tungsten dichalcogenides we chose 55 Ry/410 Ry. The Brillouin zone (BZ) integration has been performed with a Monkhorst-Pack grid\(^\text{26}\) of \(16 \times 16 \times 4\) \(k\) points and using a Gaussian broadening of 0.002 Ry \(\approx\) 27 meV. The convergence with respect to the number of \(k\) points as well as the wave-function and charge-density cutoff have been checked. The self-consistent solution of the Kohn-Sham equations was obtained when the total energy changed by less than \(10^{-9}\) Ry and the maximum force on all atoms was less than \(5 \cdot 10^{-4}\) Ry \(a_0^{-1}\) (\(a_0 \approx 0.529177\) Å is the Bohr radius). The lattice parameters thus determined are given in Tab. I and agree within 2\% with the experimental values.

The final geometry of the bulk system was used as the starting geometry for the relaxation of the layered-2D systems in an FET setup. To achieve this, the size of the unit cell was fixed in plane and the perpendicular size was increased such that the vacuum region between the repeated images was at least 23 Å. The BZ integration has been performed with a Monkhorst-Pack grid of \(64 \times 64 \times 1\) \(k\) points for the charged systems and \(16 \times 16 \times 1\) \(k\) points for the neutral ones. In order to correctly determine the Fermi energy in the charged systems, we performed a non-self-consistent calculation on a denser \(k\)-point grid of at least \(90 \times 90 \times 1\) points starting from the converged charge density. All other parameters were the same as in the calculations for the bulk systems. For the total-energy calculations of the 1T and 1T’ polytype of MoS\(_2\) and WSe\(_2\) under FET doping, we doubled the unit-cell size along one in-plane direction and correspondingly halved the number of \(k\) points along this direction.

Several methods have been developed to study electrostatics in periodic boundary condition\(^\text{24,33}\) with different experimental geometries. We used our recently developed method\(^\text{24,33}\) as it is tailored for FET setup and allows for structural optimization. The dipole for the dipole correction\(^\text{24,33}\) was placed at \(z_{\text{dip}} = d_{\text{dip}}/2\) with \(d_{\text{dip}} = 0.01\) \(L\) and \(L\) being the unit-cell size in the direction perpendicular to the 2D plane \(-\) \(L\) changed for the different calculations and was between 34 Å and 48 Å. The charged plane modeling the gate electrode\(^\text{24,33}\) was placed close to the dipole at \(z_{\text{mono}} = 0.011\) \(L\). A potential barrier with a height of \(V_0 = 2.5\) Ry and a width of \(d_{\text{b}} = 0.1\) \(L\) was used in order to prevent the ions from moving too close to the gate electrode. The final results were found to be independent of the separation of the dipole planes, as well as the barrier height and width as long as it is high or thick enough to ensure that the electron density at the position of the dipole and the gate electrode is zero, \(\rho(z_{\text{mono}}) = \rho(z_{\text{dip}}) = 0\). As we will often give the doping-charge concentration per unit cell \(n\) (i.e., in charge per unit cell, \(e/\text{unit cell}\), with the elementary charge \(e \approx 1.602 \times 10^{-19}\) C), we summarized in Tab. II the conversion to charge-carrier concentration per area \(n\) by using the experimental lattice parameters of the bulk system and the elementary charge \(e\).
(in cm\(^{-2}\)) for the different dichalcogenides and two typical doping-charge concentrations of \(n = 0.01\) e/unit cell and \(n = 0.15\) e/unit cell. Throughout the paper we will use \(n < 0\) and \(n > 0\) for electron and hole doping, respectively.

In order to calculate the Hall tensor \(R_{xy}(T; E_F)\), we used the BoltzTraP code \(^{35}\) to determine the conductivity tensors in Eqs. \(^{11}\) and \(^{12}\) (see section \(^{11}\) for more details). We fitted the band structure for each doping of the different TMDs by using 55-times more plane waves than bands and used afterwards the in-plane components of the energy-projected tensors to calculate the Hall coefficient \(R_{xyz}(T; E_F)\) for temperature \(T\) and chemical potential \(E_F\). \(R_{xyz}(T; E_F)\) is the only relevant Hall coefficient for our 2D systems assuming that the magnetic field is applied perpendicular to the layers. We checked the convergence by calculating \(R_{xyz}(T; E_F)\) with increasing number of \(k\) points and found that the results for the \(64 \times 64 \times 1\) grid and the dense grid of the non-self-consistent calculation are the same.

III. RESULTS

A. Electronic structure of TMDs

In the following we will first briefly summarize the results for the undoped TMDs before investigating the changes under field-effect doping. We focus on the changes in the valence-band maximum and the conduction-band minimum with changing transition metal or chalcogen and compare them with other results found in literature.\(^{36}\)

Figure 1 shows the band structure and the projected density of states (pDOS) for monolayer MoSe\(_2\) with and without including spin-orbit coupling (SOC). Monolayer molybdenum diselenide is (as most TMDs) a direct-bandgap semiconductor with a DFT gap of about 1.329 eV at the K point. Our calculated gap is smaller by 83 meV than the one in Ref. \(^{37}\), which can be attributed to our slightly larger in-plane lattice parameter as the size of the band gap decreases with increasing lattice constant.\(^{38-41}\)

This is due to the fact that the valence-band maximum at \(K\) is formed by in-plane states of both the transition metal and the chalcogen.\(^{42}\) On the other hand, the conduction-band minimum at \(K\) is mainly formed by out-of-plane Mo states (\(d_{z^2}\) without SOC and \(m_j = \pm 1/2\) for both \(j = 5/2\) and \(j = 3/2\) including SOC) and in-plane states of the chalcogen. The valence-band maximum near \(\Gamma\) has basically only out-of-plane states of Mo and Se as can be seen in Fig. 1. This will become very important for hole doping of the nanolayers in an FET setup – depending on which valley is doped (\(K\) or \(\Gamma\)) one can expect different doping-charge distributions. Energetically very close to the conduction-band minimum at \(K\) is a minimum half-way between \(K\) and \(\Gamma\). The corresponding point in \(k\) space is called \(Q\) in literature (sometimes \(\Lambda\) or \(\Lambda_{\text{min}}\) as it is a minimum along the \(\Lambda\) line, from \(\Gamma\) to \(K\)).

FIG. 1. (color online) Band structure and density of states projected onto atomic orbitals for monolayer MoSe\(_2\) without (upper panel) and with (lower panel) including spin-orbit coupling. As apparent in the case without SOC, mainly in-plane states contribute to the valence-band maximum near \(K\) (Mo \(d_{z^2}\) and \(d_{xy}\), Se \(p_{x/y}\)), while the maximum near \(\Gamma\) is formed by out-of-plane states (Mo \(d_{z^2}\), Se \(p_z\)). This also holds in the SOC case where the valence-band states with mainly in-plane character can be found near \(K\) (\(j = 5/2\), \(m_j = \pm 5/2, \pm 3/2\) and \(j = 3/2, m_j = \pm 3/2\) while those with more out-of-plane character can be found near \(\Gamma\) (\(m_j = \pm 1/2\) for both \(j = 5/2\) and \(j = 3/2\), see Ref. \(^{37}\) for the states in terms of spherical harmonics). On the other hand, the conduction-band minimum near \(K\) has mainly contributions from out-of-plane Mo and in-plane Se states (without SOC: Mo \(d_{z^2}\) and Se \(p_x/p_y\), with SOC: Mo \(m_j = \pm 1/2\) for both \(j = 5/2\) and \(j = 3/2\)).

FIG. 2. Band structure for bi- and trilayer MoSe\(_2\). Molybdenum diselenide changes (as all TMDs investigated in this paper) from a direct-band-gap semiconductor to an indirect one when the number of layers is increased.
even if it is not a high symmetry point of the BZ. This is also why this minimum does not lie exactly at the same point for the different TMDs and its position can even change if the number of layers is increased. The states close to the Q point have a stronger in-plane character and can thus also lead to a different doping-charge distribution if the doping occurs mainly at this point in the BZ. The same results for the character of the different valleys were also obtained in Refs. 36,42–46.

The different character of the states in the different valleys is even more important for the other TMDs. From sulfur to tellurium the difference between the minimum at K and Q decreases: for MoS$_2$ the minimum at K is lower by 279 meV while it is only 154 meV and 72 meV lower for MoSe$_2$ and MoTe$_2$, respectively. The change in the case of the tungsten dichalcogenides is much lower which however might be due to the stronger spin-orbit splitting of the bands near Q compared the splitting at K. The band structures of all undoped TMDs are summarized in the appendix, Figs. 19–23.

Increasing the number of layers in TMDs leads to a well-known change from a direct-band-gap semiconductor to an indirect one as shown in Fig. 9. The change of the direct band gap at K with increasing the number of layers is much smaller than the changes at Γ or Q. This is due to the small hybridization between different layers at K as those states have only in-plane chalcogen character. On the contrary, both valleys at Γ and Q have contributions from Se $p_z$ states. Accordingly, the maximum (minimum) at Γ (Q) shift up (down) in energy with increasing the number of layers which eventually leads to an indirect band gap between Γ and Q (see also Ref. 42 for an in-depth analyses). The transition between the indirect gap Γ $\rightarrow$ K and Γ $\rightarrow$ Q happens at different number of layers and occurs either in the bilayer case (MoSe$_2$), in the trilayer case (WS$_2$ and WSe$_2$), or in the bulk limit (MoS$_2$, MoTe$_2$). Depending on the level of theory which was used, one can also find very different results in literature when this transition occurs. Most calculations were done for MoS$_2$ for which the transition either already occurs for the bilayer or with larger number of layers. In fact, Ramasubramanian et al. have shown in Ref. 51 that using the experimental bulk distance between the layers in the bilayer case also leads to an indirect band gap Γ $\rightarrow$ Q while relaxation using PBE+D2 leads to an indirect gap Γ $\rightarrow$ K. Also for other TMDs one can find different results. For a comprehensive review of the theoretical papers see also Ref. 39 and references therein. Molybdenum ditelluride is especially peculiar, since the calculations show that its valence-band maximum is located at K even in the trilayer case. Furthermore, we find that the difference between the maximum at Γ and K is only 26 meV in bulk MoTe$_2$ which is in agreement with the experimental results in Ref. 55.

In section III D we will see that, e.g., the varying difference between the conduction-band minimum at K and Q for the different TMDs will also lead to a different thickness of the conductive channel for electron doping in an FET setup, while nearly all TMDs will behave similarly under hole doping. However, before investigating the changes under field-effect doping we want to focus on another problem which can make it difficult to dope a 2D system – the quantum capacitance.

### B. Quantum capacitance

When a 2D metallic system is contacted by a gate electrode (separated by a dielectric as shown in Fig. 3(a)), the electric field generated by the charges on the dielectric surface leads to a shift of the Fermi level of the 2D metal. This effect results in a modified capacitance with respect to the geometrical capacitance $C_{ox}$ per unit surface

$$C_{ox} = \varepsilon_{ox} \varepsilon_0 d_{ox}^{-1}, \quad (1)$$

obtained for a capacitor having a dielectric constant $\varepsilon_{ox}$ and thickness $d_{ox}$. The term “quantum capacitance” was first used by Serge Luryi in order to develop an equivalent circuit model to describe the incomplete screening of an electric field by a 2D electron gas.

As shown in Fig. 3(b), the quantum capacitance $C_Q$ is in series with that of the dielectric, namely

$$\frac{1}{C} = \frac{1}{C_{ox}} + \frac{1}{C_Q}. \quad (2)$$

Under the simplified assumption that both $C_{ox}$ and $C_Q$ are independent of the applied gate voltage $V_G$, the charge induced in the 2D system $n_Q$ can be written as:

$$n_Q = \begin{cases} 0 & \forall V_G \in (V_V, V_c) \\ C (V_c - V_G) & \forall V_G < V_c \\ C (V_V - V_G) & \forall V_G > V_c \end{cases}, \quad (3)$$

where $V_V$ and $V_c$ are the onset potentials to fill the valence-band minimum or conduction-band maximum, respectively. Thus, when $C_Q \gg C_{ox}$, we have

$$C = C_{ox} \left(1 + \frac{C_{ox}}{C_Q}\right)^{-1} \approx C_{ox}. \quad (4)$$

![FIG. 3. (a) Schematic illustration of an FET setup in which the 2D metallic system is separated from the gate electrode by a dielectric with dielectric constant $\varepsilon_{ox}$ of thickness $d_{ox}$. (b) Equivalent circuit for the overall capacitance seen at the gate electrode.](image-url)
TABLE III. Geometrical capacitances for parallel-plate capacitors with 100 nm SiO$_2$ (relative permittivity $\varepsilon_r = 3.9$), 10 nm HfO$_2$ ($\varepsilon_r \approx 20$), and an 1 nm thick ionic-liquid (IL) FET ($\varepsilon_r \approx 15$), quantum capacitance for electron doping of the K valley ($m \approx 0.5m_0$) and hole doping of the $\Gamma$ valley ($m \approx m_0$) of MoS$_2$ ($\nu = 4$), and the overall capacitance of a setup as shown in Fig. 3(b). All capacitances are given in units of $\mu$F cm$^{-2}$.

|             | $C_{\text{Q}}^x$ | $C_{\text{Q}}^z$ |
|-------------|-----------------|-----------------|
| SiO$_2$     | $0.035$         | $0.035$         |
| HfO$_2$     | $1.771$         | $1.759$         |
| IL          | $13.28$         | $12.65$         |

and we regain the classical result, i.e., the charge which can be induced in the 2D system depends only on the applied gate voltage and the capacitance between gate and sample.

A prominent example in which the quantum capacitance can be comparable to the geometrical, $C_Q \approx C_{\text{ox}}$, and thus lead to deviations from the classical picture is graphene – due to its linear dispersion relation at the K points the charge which can be induced in an FET setup is much smaller than the corresponding charge at the gate electrode. Similarly, the quantum capacitance in nanolayers of TMDs could also reduce the amount of induced charge. Yet, in the case of TMDs the dispersion relation is not linear but can be approximated by a quadratic band for small doping. As shown in Refs. 50, 59, the quantum capacitance in this case and for gate voltages larger (smaller) than the onset potential of the conduction band (valence band) is given by

$$C_Q = \frac{g_s g_v m q^2}{\pi \hbar^2},$$

where $g_s$ and $g_v$, $m$, and $q$ are the spin and valley degeneracies, the effective mass, and the charge, respectively. Depending on (i) the dielectric thickness $d_{\text{ox}}$, (ii) the effective mass of the 2D metallic system, and (iii) the number of valleys $\nu = g_s g_v$, the quantum capacitance $C_Q$ can be relevant or not.

Table I shows the total capacitance, geometrical capacitance for typical gate dielectrics, and the quantum capacitance for electron doping of the K valley or hole doping of the $\Gamma$ valley of MoS$_2$ (the effective masses of the different valleys were taken from Ref. 39). As the geometrical capacitance of a parallel-plate capacitor increases with decreasing thickness of the dielectric, an ionic-liquid (IL) FET with an 1 nm thick electric double layer (inner Helmholtz plane) shows the largest deviation of the total capacitance $C$ from the geometrical capacitance $C_{\text{IL}}$ – even for a thin dielectric layer of 10 nm HfO$_2$, $C \approx 0.986 C_{\text{HfO}_2}$. Yet, for TMDs the number of valleys increases with increasing doping (valleys at K and Q or K and $\Gamma$ for electron or hole doping, respectively), which also leads to a considerably larger DOS at the Fermi energy than for a single quadratic band. Thus, the quantum capacitance $C_Q$ is further increased which in turn leads to $C \approx C_{\text{ox}}$.

C. Structural changes under field-effect doping

The doping via FET setup has only a minor influence on the structure of the TMDs – the changes are much smaller than for, e.g., ZrN$_2$. This is due to the weak polarity of the bond between the transition-metal and the chalcogen. The largest change can be found for the layer thickness ($z$ component of the chalcogen–chalcogen vector) of the layer closest to the charged plane representing the gate electrode – the layer thickness increase by $0.06 \text{ Å}$ for a large electron doping of $n = -0.3 \text{ e/} \text{unit cell}$ ($n \approx -3.16 \times 10^{14} \text{ cm}^{-2}$) and decreases by $0.02 \text{ Å}$ for a large hole doping of $n = +0.3 \text{ e/} \text{unit cell}$. This change is mainly due to the increase/decrease of the chalcogen–transition-metal bond length of those being closest to the gate – we find $0.04 \text{ Å}$ for $n = -0.3 \text{ e/} \text{unit cell}$ and $0.02 \text{ Å}$ for $n = +0.3 \text{ e/} \text{unit cell}$. Additionally, there is also a small change in the angle between the first chalcogen, the transition-metal, and the second chalcogen of up to $0.9^\circ$ ($-0.4^\circ$) for large electron (hole) doping. Note that even if the structural changes seem to be small it is still important to relax the system in the FET setup. Otherwise, the band structure can be quite different for doping $|n| > 0.15 \text{ e/} \text{unit cell}$ as exemplified in Fig. 24 in the appendix.

Even if the internal structure changes only slightly under FET doping, electron doping could induce a phase transition where the structure of the full nanolayer system is altered. It is well known that lithium, or...
potassium intercalated MoS$_2$ can undergo a phase transition in which the Mo coordination changes from a direct-band-gap, semiconducting, trigonal-prismatic structure (labeled 2H, "2H" as there are two layers in the unit cell) to a metallic, octahedral one (1T). It has been found experimentally and shown theoretically, that also monolayer MoS$_2$ can undergo this phase transition. In the calculations, for a high electron doping by H (Ref. 65) or Li (Ref. 66) adsorption of $n \approx -0.35$ e/unit cell or $n = -0.44$ e/unit cell, respectively, the octahedral phases such as the 1T or 1T’ phases become more stable than the 1H phase. In the 1T’ phase the molybdenum forms zig-zag chains like tungsten in WTe$_2$.67,72 Such a transition was also found experimentally by rhenium doping of WS$_2$ nanotubes and monolayer MoS$_2$, and by transfer of hot electrons generated in gold nanoparticles to monolayer MoS$_2$. In order to determine if the FET setup can lead to such a phase transition for electron doping, we compare in Fig. 3 the total energy for the monolayer structures of 1T-MoS$_2$ and 1T’-MoS$_2$ ($E_{1T-MoS_2}^{tot}$) with the total energy of the 1H polytype ($E_{1H-MoS_2}^{tot}$). We find that the 1T’ structure becomes more stable for electron doping larger than $n = -0.35$ e/unit cell in close agreement with the results of Refs. 65,66. Thus, it seems that the interaction between the H/Li atoms and the MoS$_2$ layer has only a minor influence on the phase stability as the transition occurs in our FET setup at the same doping. We also calculated the energy difference between 1T’-WS$_2$ and 1H-WS$_2$, ($E_{1T’-WS_2}^{tot} - E_{1H-WS_2}^{tot}$), for few electron-doping concentrations and found that for a concentration of $n = -0.35$ e/unit cell the 1T’ polytype becomes more stable by 63meV. In the following, we will thus consider only electron doping of the H polytype with $n \geq -0.35$ e/unit cell as it is the most stable structure found in nature and is often used to prepare the samples by the mechanical-cleavage method.

D. Band structure in FET setup

In the following section, we want to investigate the influence of field-effect doping on the electronic properties of the TMDs. The doping via FET setup changes the band structure considerably as exemplified in Figs. 4 and 5 which show the band structures for different electron and hole doping levels for mono- and trilayer MoS$_2$, respectively. In the appendix we also demonstrate that it is important to correctly model the FET setup by comparing the band structures of mono- and trilayer MoS$_2$ calculated with a compensating jellium background to those calculated with our method (Figs. 25, 26). Furthermore, we also provide the band structures for more doping levels and all the other TMDs in the appendix (in total more than 250 calculations, Figs. 27–62). We summarized the evolution of the band structure with increasing doping in the left panel of Figs. 6 which show the position of the different band extrema with respect to the Fermi energy. Additionally, the right panel in those figures shows the relative amount of doping charge per valley given by

$$n_\alpha = \frac{e}{N_\alpha} \sum_{k \in \Omega_\alpha} \sum_{i} |\psi_{i,k}|^2. \tag{6}$$

Here $\alpha = \{\Gamma, K, Q\}$, $\Omega_\alpha$ defines the subset of k points which are closer to, e.g., $\Gamma = \Gamma$ than to any $\alpha \neq \Gamma$, $N_\alpha$ is the total number of those k points, and $\varepsilon_{i,k}$ is the eigenenergy for band i at k. The interval $[\varepsilon_1, \varepsilon_2]$ is always chosen such that the probability density is integrated between an energy within the former band gap $E_{m}$ and the Fermi energy $E_F$ of the doped system, i.e., $[E_F, E_m]$ and $[E_m, E_F]$ for hole and electron doping, respectively.

Electron doping

For n-type doping of monolayer MoS$_2$ (as for all monolayer TMDs) the doping charge first occupies the extremal K point at K. For small doping (as long as only one valley is doped) the bands are rigidly shifted. However, as soon as a second valley is close to the Fermi energy, the doping cannot be described by a rigid shift of the bands anymore. For electron doping, the down shift of the bands at K slows down and, as the valley at Q starts to get occupied, is eventually reversed into an up shift. Finally, for high electron doping, the K valley is unoccupied again and the doping charge is solely localized around Q. Comparing our results of the changes in the conduction band for electron doping of monolayer MoS$_2$ (Figs. 5, 7) with literature shows that it is important to correctly model the system – while the authors of Ref. 76 find an up shift of the Q valley with increasing electron doping, we see a down shift. The opposite shift in Ref. 77 might be due to the free-electron states at $\Gamma$ (i.e., the states in the vacuum between the repeated images, cf., also Ref. 77) which approach the Fermi energy with increasing doping. Also the authors of Refs. 20,23,77 find a down shift of the Q valley further supporting our results even if in those works the asymmetric electric field in an FET has not been taken into account. The amount of doped electrons needed to have the charge completely localized at Q depends on the TMD (i.e., the initial energy difference between the minimum at K and Q) and is larger than $n = -2.2 \times 10^{14} \text{cm}^{-2}$ ($n \approx -0.2$ e/unit cell): the transition occurs for MoS$_2$ at $n \approx -3.83 \cdot 10^{14} \text{cm}^{-2}$, for MoSe$_2$ at $n \approx -2.5 \cdot 10^{14} \text{cm}^{-2}$, for MoTe$_2$ at $n \approx -2.22 \cdot 10^{14} \text{cm}^{-2}$, for WS$_2$ at $n \approx -3.41 \cdot 10^{14} \text{cm}^{-2}$, and for WSe$_2$ at $n \approx -3.31 \cdot 10^{14} \text{cm}^{-2}$.

In multilayer MoS$_2$, WS$_2$, and WSe$_2$ first the valley at K is doped and both valleys at K and Q are occupied until $n \approx -3.3 \cdot 10^{14} \text{cm}^{-2}$. On the contrary, in bi- and trilayer MoSe$_2$ and MoTe$_2$ the order is reversed: electrons first occupy the valley at Q and the doping at K is always smaller. This is due to the minimum at Q being lower in energy than the one at K in the undoped system (see Figs. 8). For a doping of $n \lesssim -2.1 \cdot 10^{14} \text{cm}^{-2}$ for
FIG. 5. Band structure for different FET induced doping of monolayer MoS$_2$. The figures in the left column are for electron doping while the right column shows the hole doping case. For monolayer MoS$_2$ mainly the valleys at K are filled and only for a high doping of $n \approx \pm 1.69 \cdot 10^{14}$ cm$^{-2}$ ($n = \pm 0.15 \, \text{e/} \text{unit cell}$) a small amount of charge is in the maximum at Γ (hole doping) or in the minimum at Q (electron doping). The band structures for more doping levels and all the other TMDs can be found in the appendix (Figs. 27–62).

MoSe$_2$ the K valley is even unoccupied. Yet, one can expect that for small electron doping ($|n| < 10^{13}$ cm$^{-2}$) of thick samples (more than 3 layers) of MoS$_2$, WS$_2$, and WSe$_2$ the electrons will also first occupy the Q valley as this valley is lowered in energy with increasing number of layers.

Hole doping

For p-type doping of the monolayer TMDs, the doping charge first occupies the extrema at K. However, in contrast to the electron-doping case, in the high-hole-doping limit ($n > +0.2 \, \text{e/} \text{unit cell}$, $n \gtrsim +2.1 \cdot 10^{14}$ cm$^{-2}$) of the monolayer TMDs both valleys at Γ and K are occupied – the relative amount of doping charge in the Γ valley is even higher than that in K. The transition when the Γ valley is more occupied than the K valley again depends on the TMD, i.e., on the initial energy difference between the valence-band maxima. In the case of MoS$_2$ for example even a small doping is enough to dope more the Γ valley. Only exception from this picture is MoTe$_2$ for which always K is more occupied even for $n = +0.35 \, \text{e/} \text{unit cell}$ ($n \approx +3.23 \cdot 10^{14}$ cm$^{-2}$, cf., Fig. 9).
Trilayer MoS$_2$

![Band structure for different FET induced doping of trilayer MoS$_2$.](image)

**FIG. 6.** Band structure for different FET induced doping of trilayer MoS$_2$. The figures in the left column are for electron doping while the right column shows the hole doping case. In contrast to the monolayer case, the doping at Γ/Q (hole/electron doping) is more important in trilayer MoS$_2$. The band structures for more doping levels and all the other TMDs can be found in the appendix (Figs. 27–62).

Hole doping of the bilayer and trilayer TMDs is again very similar: in all investigated compounds (except MoTe$_2$) first the conduction-band maximum at Γ is occupied, while for higher doping also K starts to get filled. Most interestingly, in some cases the second band at K is never occupied. For trilayer WS$_2$ and WSe$_2$ it is even pushed down in energy, effectively increasing the splitting of the spin-orbit-split bands. For WSe$_2$ it is possible to achieve even higher hole-doping concentrations than shown in Fig. 11 by using an IL-FET. We thus calculated for trilayer WSe$_2$ also some higher doping cases (up to $n = +1 \text{ e/}\text{unit cell}$, or $n ≈ +1 \cdot 10^{15} \text{ cm}^{-2}$) in order to understand what might happen for such a high doping. Our calculated band structure is very different from the one in Ref. 16 which was calculated without proper treatment of the FET setup. For a doping of one hole per unit cell the second band at K is pushed down below the Fermi energy and also the first band at K is lowered. The band structure in Fig. 12 shows that the former band gap is closed and the first two bands are nearly unoccupied. However, since these are bands localized on the first layer close to the gate, we believe that for such a high doping the ions of the ionic liquid might start to interact with WSe$_2$. In our simplified model without inclusion of the full dielectric it is difficult to proof this statement and we will thus leave this interesting problem for future investi-
Conductive channel

Another important property in order to understand different experiments on FET doping on TMDs is the doping-charge layer thickness, i.e., the size and shape of the conductive channel created and influenced by the gate voltage. To visualize the conductive channel we calculated the planar-averaged doping-charge distribution along $z$,

$$\rho_{dop}^\parallel (z) = \frac{e}{\Omega_{2D} N_k} \int dA \sum_{i, k} |\psi_{i, k}(r)|^2$$

Here $\Omega_{2D}$ is the unit cell area and $N_k$ is the total number of $k$ points. The interval $[\varepsilon_1, \varepsilon_2]$ is defined as above, i.e., $[E_F, E_m]$ and $[E_m, E_F]$ for hole and electron doping, respectively. This property not only reveals the thickness of the conductive channel but also the relative distribution among the different layers.

In our calculations for low hole doping the charge is nearly evenly distributed between the first two layers with only small contributions at the third layer as can be seen in the upper panel of Fig. 13. Increasing the doping (i.e., increasing the gate voltage, lower panel of Fig. 13) the charge is more and more localized on the layer closest to the gate with a negligible amount of holes on the third layer. In the case of electron doping of multilayer MoS$_2$, the charge is localized on the first layer as only the $\Gamma$ valley is doped (small contribution of the out-of-plane states of sulfur). Only for higher doping when the minimum at $Q$ is occupied a small amount of charge can be found on the second layer (cf., lower panel of Fig. 13 and right panel of Fig. 7). One can also see that the asymmetry in the doping-charge distribution is more pronounced for hole doping and that the system in this case moves closer to the dielectric. Furthermore, for low hole doping the doping charge on the second layer is even slightly larger than the one on the first.

Figure 14 summarizes the doping-charge distribution for all bi- and trilayer TMDs. In the hole-doping case all TMDs behave similar except MoTe$_2$: for low doping the holes are delocalized over the first two layers with only small contributions in the third layer and, thus, the bi- and trilayer systems are nearly the same. Increasing the doping leads to stronger localization of the charge within the first layer and an effective narrowing of the conductive channel. One can also easily understand why MoTe$_2$ behaves differently: in all multilayer TMDs first the valley at $\Gamma$ is doped, since it is the valence-band maximum,
FIG. 8. Position of the different band minima/maxima $E_i$ (left panel) with respect to the Fermi level and relative amount of doping charge per valley $n_{\alpha}$ (right panel) as function of doping for mono-, bi-, and trilayer MoSe$_2$. “Q” labels the conduction-band minimum half-way between K and $\Gamma$. In each graph, the scale and the units for the lower $x$ axis are given in the lowest graph, while those of the upper $x$ axis are given in the uppermost graph. Lines are guides for the eye.

FIG. 9. Position of the different band minima/maxima $E_i$ (left panel) with respect to the Fermi level and relative amount of doping charge per valley $n_{\alpha}$ (right panel) as function of doping for mono-, bi-, and trilayer MoTe$_2$. “Q” labels the conduction-band minimum half-way between K and $\Gamma$. In each graph, the scale and the units for the lower $x$ axis are given in the lowest graph, while those of the upper $x$ axis are given in the uppermost graph. Lines are guides for the eye.
FIG. 10. Position of the different band minima/maxima $E_i$ (left panel) with respect to the Fermi level and relative amount of doping charge per valley $n_\alpha$ (right panel) as function of doping for mono-, bi-, and trilayer WS$_2$. “Q” labels the conduction-band minimum half-way between K and Γ. In each graph, the scale and the units for the lower x axis are given in the lowest graph, while those of the upper x axis are given in the uppermost graph. Lines are guides for the eye.

FIG. 11. Position of the different band minima/maxima $E_i$ (left panel) with respect to the Fermi level and relative amount of doping charge per valley $n_\alpha$ (right panel) as function of doping for mono-, bi-, and trilayer WSe$_2$. “Q” labels the conduction-band minimum half-way between K and Γ. In each graph, the scale and the units for the lower x axis are given in the lowest graph, while those of the upper x axis are given in the uppermost graph. Lines are guides for the eye.
while in MoTe$_2$ the K valley is the maximum. As we have seen in section IIIA the states close to Γ have large out-of-plane contributions of both the transition metal and the chalcogen atom, while the valley at K is composed only of in-plane states. Increasing the hole doping however also leads for MoTe$_2$ to a small doping of the Γ valley. Thus, the amount of charge within the second layer increases slightly in the beginning. The small kink for trilayer MoTe$_2$ close to $n = +0.46 \cdot 10^{15}$ cm$^{-2}$ is due to both bands at Γ and K being close to the Fermi energy. In this low doping limit (per valley) the calculation would require an infinite number of k points to fully converge the results. Further increase of the doping leads as for all TMDs to a larger screening of the electric field and therefore to the stronger localization within the first layer as can also be seen in the lower panel Fig. 13.

For electron doping we can divide the different TMDs into two different classes: (i) those in which the conductive channel for low doping ($n \approx -10^{13}$ cm$^{-2}$) has a thickness of just one layer (MoS$_2$, WS$_2$, WSe$_2$) and (ii) those with a three-layer-thick channel (MoSe$_2$, MoTe$_2$). Using the results of Figs. 7-11 one can see that in the TMDs...
of class (i) initially the K valley is doped while in (ii) the Q valley is occupied. Since the chalcogen states close to the conduction-band minimum at K have mainly in-plane character (in contrast to the transition-metal states which have $d_{z^2}$ character), the hybridization between the layers is small and the electrons are more localized within the first layer. On the contrary, the chalcogen states close to Q have a large out-of-plane contribution which leads to a stronger hybridization between the layers. With increasing doping the electric field of the gate is more and more screened and the size of the conductive channel reduces to one layer. Furthermore, one can also understand why the tungsten dichalcogenides have a steep increase of the channel thickness in the beginning while this is not the case for MoS$_2$: firstly, the difference between the conduction-band minimum at K and Q is much smaller in multilayer WS$_2$/WSe$_2$ than in MoS$_2$ and secondly, a small electron doping can also result in an effective separation of the single (doped) layer from the multilayer system. The difference between the conduction-band minimum at K and Q for monolayer MoS$_2$ is however twice as large as in the tungsten systems ($\approx 300$ meV for MoS$_2$ and $\approx 150$ meV for WS$_2$/WSe$_2$). Thus, the valley at the Q point is much earlier doped in WS$_2$/WSe$_2$ than in MoS$_2$.

**Number of occupied bands**

It is important to note, that the thickness of the doping-charge distribution, the number of occupied bands at a given $k$ point, and the number of TMD layers (i.e., the system size) are uncorrelated. Indeed, as can be seen in Fig. 15, the total spin-valley degeneracy $\nu$ can be quite similar for different number of layers, whereas the doping charge is localized on one or two layers as seen in the previous section. Here the total spin-valley degeneracy has been calculated by counting the number of valleys within the interval $[\varepsilon_1, \varepsilon_2]$ as defined above:

\[
\nu = \sum_{\alpha} \nu^\alpha = \sum_{\alpha} g^\alpha_s g^\alpha_v.
\]

Here $g^\alpha_s$ and $g^\alpha_v$ are the spin and valley degeneracies of the valley at $k$ point $\alpha = \{\Gamma, K, Q\}$. For electron doping $\nu$ is much higher than in the hole doping case as the valley degeneracy for the conduction-band minimum close to Q is $g^\nu_s = 6$ (spin degeneracy $g^\nu_v = 1$). Thus, as soon as the valley at Q is doped, $\nu$ increases drastically by 6 or 12 depending on whether only one or both spin-orbit-split bands are filled. For some TMDs a high electron doping of $n < -3.5 \cdot 10^{14}$ cm$^{-2}$ leads to a large lowering of the minimum at Q – so much that it is actually not a valley anymore but a ring around $\Gamma$. This can be seen by the minimum between $\Gamma$ and M which appears in the band structure (cf., Figs. 15 and 16) and band structures in the appendix). In this case, we do not count it as six independent valleys but as one.

On the contrary, for high hole doping $(n > +2 \cdot 10^{14}$ cm$^{-2}$) of multilayer TMDs the number of occupied valleys is either $\nu = 6$ or $\nu = 8$ as only bands at K ($g^v_v = 2$, $g^v_s = 1$) and $\Gamma$ ($g^v_v = 1$, $g^v_s = 2$) are doped. In the monolayer systems often two valleys are doped – the valence-band maximum at K and either the second spin-orbit-split band at K or the valence-band maximum at $\Gamma$. Accordingly, the difference between the valence-band maximum at K and at $\Gamma$ determines the doping-charge concentration needed in order to dope two valleys.

![Figure 15](image_url)
at different points in the BZ. The spin-degenerate maximum at $\Gamma$ is occupied for monolayer MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$ for hole doping larger than $+1 \cdot 10^{13}$ cm$^{-2}$, $+5 \cdot 10^{13}$ cm$^{-2}$, $+2 \cdot 10^{13}$ cm$^{-2}$, and $+8 \cdot 10^{13}$ cm$^{-2}$, respectively. Again monolayer MoTe$_2$ is exceptional due to the large difference of $\approx 600$ meV between the maximum at K and $\Gamma$. Just for a very high hole doping of $n \approx +3.23 \cdot 10^{14}$ cm$^{-2}$ ($n = +0.35$ electrons/unit cell) the second band at K is occupied and a “ring” around and close to $\Gamma$ appears (which is again counted as 1).

Up to now we have focused on the changes in the electronic structure of the different TMDs with increasing doping and we saw that for, e.g., high electron doping the charge is mainly localized around the Q point. We now want to investigate how the amount of doping charge and thus the number of occupied bands and the thickness of the conductive channel is determined experimentally.

### E. Hall-effect measurements

In order to determine the doping charge in a sample, one commonly performs a Hall experiment as the inverse Hall coefficient is directly proportional to the charge-carrier density $n$ in the case of parabolic, isotropic bands. This, however, is already a crude approximation which, as we will see below, can lead to large differences between the charge-carrier density thus calculated and the real density within the sample.

We closely follow the work of Madsen and Singh$^{35}$ and sketch the calculation of the Hall coefficient (or more specifically, the Hall tensor $R_{ijk}$) within Boltzmann transport theory. In presence of an electric field $\mathbf{E}$ and a magnetic field $\mathbf{B}$, the electric current $\mathbf{j}$ can be written as

$$j_\alpha = \sigma_{\alpha\beta} E_\beta + \sigma_{\alpha\beta\gamma} E_\beta B_\gamma + \cdots,$$  

with the conductivity tensors $\sigma_{\alpha\beta}$ and $\sigma_{\alpha\beta\gamma}$, and the indices denoting the spatial dimensions. Here and henceforth, we will always adopt Einstein’s sum convention, according to which whenever an index occurs twice in a single-term expression, the summation is carried out over all possible values of this index. The Hall tensor is defined as

$$R_{ijk} (T; E_F) = \frac{E_j^\text{ind}}{j_k^\text{appl} B_k^\text{appl}} = (\sigma^{-1})_{\alpha j} \sigma_{\alpha\beta k} (\sigma^{-1})_{i\beta},$$

where $E_j^\text{ind}$ is the electric field along direction $j$ which is induced by the applied magnetic field $B_k^\text{appl}$ and current $j_k^\text{appl}$ along direction $k$ and $i$, respectively.

Within the relaxation-time approximation the conductivity tensors $\sigma_{\alpha\beta}$ and $\sigma_{\alpha\beta\gamma}$ for temperature $T$ and chemical potential $E_F$ are given in the 2D case by$^{35}$

$$\sigma_{\alpha\beta} (T; E_F) = \frac{q^2}{(2\pi)^2} \int \tau_{\alpha\beta} (\varepsilon, \mathbf{k}) \frac{\partial f_{E_F} (T; \varepsilon, \mathbf{k})}{\partial \varepsilon} d^2 \mathbf{k},$$

$$\sigma_{\alpha\beta\gamma} (T; E_F) = \frac{q^3}{(2\pi)^2} \int \tau_{\alpha\beta\gamma} (\varepsilon, \mathbf{k}) \frac{\partial f_{E_F} (T; \varepsilon, \mathbf{k})}{\partial \varepsilon} (M_{\beta\gamma})^{-1} d^2 \mathbf{k}.$$  

Here, $q = \pm e$ is the charge of the charge carriers in band $\varepsilon_{\alpha\beta}$ with momentum $\mathbf{k}$, $f_{E_F} (T; \varepsilon)$ is the Fermi function $\frac{\exp[(\varepsilon - E_F)/(k_B T)] + 1}{\exp[(\varepsilon - E_F)/(k_B T)] + 1}$, and $\varepsilon_{\gamma\nu\mu}$ is the Levi-Civita symbol. The relaxation time $\tau_{\alpha\beta\gamma}$ in principle is dependent on both the band index $\alpha$ and the $\mathbf{k}$ vector direction. Furthermore, $v_{\alpha\beta}^i$ is the group velocity

$$v_{\alpha\beta}^i = \frac{\hbar}{\partial \varepsilon_{\alpha\beta}}$$

and $(M_{\beta\gamma})^{-1}$ the inverse mass tensor

$$\left(M_{\beta\gamma}^{-1}\right)^{-1} = \frac{1}{\hbar^2} \frac{\partial^2 \varepsilon_{\alpha\beta}}{\partial k_\alpha \partial k_\alpha}.$$  

To show that the inverse Hall coefficient $R_{xyz}$ is proportional to $n$, we start by assuming bands with quadratic dispersion. The dispersion relation for a quadratic, isotropic band in 2D is given by

$$\varepsilon_{i\beta} (\mathbf{k^\text{ind}}, \mathbf{k^\text{appl}}) = \frac{\hbar}{2m_i} k_i^2,$$

with $k_i^2 = k_x^2 + k_y^2$. The group velocity is then $v_{i\beta}^\text{ind} = \hbar k_i/m_i$ while the mass tensor in Eq. (14) is for each band a diagonal matrix with $m_i^{-1}$ on the diagonal. In the zero temperature limit and assuming an $i$- and $\mathbf{k}$-independent relaxation time $\tau_{i\beta} = \tau (E_F)$ the conductivity distributions in Eqs. (11) and (12) are given by

$$\sigma_{\alpha\beta} (0; E_F) = \sum_i \frac{\tau}{m_i} n_i,$$

$$\sigma_{\alpha\beta\gamma} (0; E_F) = - \sum_i \frac{q^3}{m_i} \varepsilon_{\beta\gamma} n_i,$$

where $n_i$ is the charge-carrier density in band $i$. Finally, assuming that the magnetic field is applied perpendicular to the 2D system along $z$, we get for the Hall coefficient

$$R_{xyz} (0; E_F) = \sum_i \frac{n_i m_i^2}{m_i} \frac{n_i}{q (\sum m_i^{-1} n_i)^2}.$$  

Thus, only for valley-independent effective mass $m_i = m$ the inverse Hall coefficient is directly proportional to the doping-charge concentration $n = n \cdot q$. The results in
Figure 16. Ratio of the inverse Hall coefficient $R_{xyz}^{-1}$ to the doping charge $n$ as function of doping for the mono- (black, solid), bilayer (red, dashed), and trilayer (green, dash-dotted) of all investigated TMDs for a temperature of $T = 300$ K. Note also the different range of the ordinate in the case of MoTe$_2$.

Eqs. (16), (17), and (18) also hold for a 3D system, however with the important difference that the conductivity in two dimensions is independent of the mass of the charge carriers, since the density $n$ is proportional to $m$. Furthermore, the Hall coefficient is inversely proportional to the mass $m$ in the 2D case.

In the constant-relaxation-time approximation ($\tau_{i,k} = \tau(E_F)$) and for hexagonal symmetry (such as in the TMDs), the Hall tensor in Eq. (10) has only two independent coefficients (in-plane and out-of-plane component). However, it is important to remember that this simple equation for the Hall coefficient $R_{xyz}$, Eq. (18), is only valid as long as there are only bands with isotropic, quadratic dispersion and if $\tau_{i,k} = \tau(E_F)$. For small doping this might be a good approximation but in the high doping case this approximation can break down – especially, as soon as a minimum/maximum with non-quadratic dispersion starts to get filled.

Figure 17 shows the ratio of the inverse Hall coefficient $R_{xyz}^{-1}(T; E_F)$ (calculated with the BoltzTraP code using Eqs. (10) (12) and assuming $\tau_{i,k} = \tau(E_F)$) to the doping-charge concentration $n$, as a function of doping for the mono-, bi-, and trilayer systems for $T = 300$ K. The comparison between $T = 0$ K and $T = 300$ K which can be found in the appendix, Figs. 63–65, shows that the temperature has only a minor influence on the inverse Hall coefficient except for MoTe$_2$ (which we will also discuss separately).

For most of the studied systems, the inverse Hall coefficient $R_{xyz}^{-1}(300$ K; $E_F)$ shows a strong deviation from the doping charge $n$ for large doping – the doping-charge concentration calculated using the inverse Hall coefficient can be 1.5 times larger than the real concentration. In fact, $R_{xyz}^{-1}(300$ K; $E_F) \approx n$ is true only in two cases (cf., Eq. (18)): either (i) if mainly one valley with parabolic dispersion is doped or (ii) if the doping charge is split between several valleys with quadratic bands which however have similar effective masses.

Case (i) holds only for small hole doping ($n < \sim +5 \cdot 10^{13} \text{cm}^{-2}$) of all multilayer TMDs as mainly the $\Gamma$ val-
ley is doped. The deviation of the inverse Hall coefficient from the doping charge n increases with increasing doping of the valence-band maximum at K. Accordingly, \( R_{\text{xy}}^{-1}(300 \text{ K}; E_F) \approx n \) for a larger range of hole doping of multilayer MoS\(_2\) than in other TMDs as the doping at K is negligible. For high hole doping (\( n \approx 2 \cdot 10^{14} \text{ cm}^{-2} \)) the deviation is due to the non-parabolicity of the bands near K. If however the charge is split between \( \Gamma \) and K the difference can be explained by the much larger effective mass of the \( \Gamma \) valley (i.e., in variance with case (ii)). Assuming \( n_\Gamma = n_K = n/2 \), Eq. (18) simplifies to

\[
R_{\text{xy}}^{-1}(0; E_F) = \frac{1}{2} \frac{m_\Gamma m_K}{m_\Gamma^2 + m_K^2},
\]

which is always smaller than 1 for \( m_\Gamma \neq m_K \). This also explains why the inverse Hall coefficient approaches \( 0.7 \) for small hole doping of monolayer MoS\(_2\). At \( T = 300 \text{ K} \) \( n \) is split between both maxima which have however very different masses \( m_\Gamma = 3.524 m_0 \) and \( m_K = 0.637 m_0 \).

On the contrary, the agreement between \( R_{\text{xy}}^{-1}(300 \text{ K}; E_F) \) and \( n \) is much better for electron doping up to \( n \approx -2 \cdot 10^{14} \text{ cm}^{-2} \) even if both conduction-band minima at K and Q are occupied. This is due to the similar effective masses of those two valleys. As in the hole-doping case the difference between \( R_{\text{xy}}^{-1}(300 \text{ K}; E_F) \) and \( n \) increase for larger doping (\( n \lesssim -2 \cdot 10^{14} \text{ cm}^{-2} \)) which is due to the increasing non-parabolicity of the bands.

The only case where the model of a 2D electron gas with constant relaxation time gives reasonable results for the doping-charge concentration within a large range of both electron and hole concentrations is multilayer MoS\(_2\). Since the agreement between \( R_{\text{xy}}^{-1}(T; E_F) \) and \( n \) can be much better in other systems as exemplified for CoSb\(_3\) in Ref. 33, the deviations shown in Fig. 16 point out problems if the specific band structure is not taken into account. Once again, MoTe\(_2\) is particularly interesting because the inverse Hall coefficient \( R_{\text{xy}}^{-1}(300 \text{ K}; E_F) \) is nearly three times bigger than \( n \) for a hole doping of \( n \approx +1.4 \cdot 10^{14} \text{ cm}^{-2} \).

In order to understand the origin of this behavior of \( R_{\text{xy}}^{-1}/n \) for hole doping of monolayer MoTe\(_2\), we plot \( R_{\text{xy}} \) as function of temperature in Fig. 17. As the temperature is reduced, the Hall coefficient \( R_{\text{xy}}(T; E_F) \) decreases and for \( T \leq 50 \text{ K} \) it even changes the sign. The result for \( T = 50 \text{ K} \) in Fig. 17 indicates that in the range of \( +1.25 \cdot 10^{14} \text{ cm}^{-2} \leq n \leq +1.5 \cdot 10^{14} \text{ cm}^{-2} \) the Hall coefficient \( R_{\text{xy}} \) changes twice the sign. The band structure for a doping of \( n \approx +1.48 \cdot 10^{14} \text{ cm}^{-2} \) (inset in Fig. 17) shows that the valence band has at least two inflection points close to the K point which cross the Fermi energy with increasing doping. Accordingly, the effective mass changes the sign and thus also the conductivity tensor \( \sigma_{\alpha\beta} \) and \( R_{ij\kappa} \). Furthermore, the nearly linear dispersion along \( K \rightarrow \Gamma \) leads to \( m \rightarrow 0 \) and thus to the large difference between \( R_{\text{xy}}^{-1} \) and \( n \). For bi- and trilayer MoTe\(_2\) the deviations are smaller and at higher doping values. This is due to the finite contribution of the doping charge at the \( \Gamma \) point which leads to a smaller doping around K.

F. Conductivity and DOS at the Fermi energy

In the end, we want to briefly analyze the DOS at the Fermi energy \( E_F \) and the in-plane conductivity \( \sigma_{xx}/\tau \) in Fig. 18. Both were calculated using the fitted band structure of BoltzTraP. The DOS at the Fermi energy \( E_F \) in the left-hand panel shows, that the doping charge cannot always be described with quadratic, isotropic bands in 2D (as also shown above by the behavior of \( R_{\text{xy}}^{-1} \)). In this case, DOS(\( E_F \)) would be constant and would have steps as soon as another band crosses \( E_F \). In fact, DOS(\( E_F \)) has steps and those can be related to crossing bands, but for high doping it can deviate from a simple 2D electron gas.

For hole doping of monolayer MoS\(_2\), MoSe\(_2\), WS\(_2\), and WSe\(_2\) the DOS at the Fermi energy is nearly constant as soon as the \( K \) valley is doped, i.e., for doping larger than \( n \approx +0.1 \cdot 10^{14} \text{ cm}^{-2} \), \( n \approx +1.5 \cdot 10^{14} \text{ cm}^{-2} \), \( n \approx +0.5 \cdot 10^{14} \text{ cm}^{-2} \), and \( n \approx +0.9 \cdot 10^{14} \text{ cm}^{-2} \), respectively. Also for hole-doping smaller than \( n \leq +1.1 \cdot 10^{14} \text{ cm}^{-2} \) of multilayer MoS\(_2\) the DOS is constant as only the \( K \) valley is doped in this regime. The non-constant behavior for hole doping of the other multilayer systems increases with increasing doping of the \( K \) valley: it is more pronounced for MoSe\(_2\) and WSe\(_2\) than for MoS\(_2\) and WS\(_2\) (cf., Figs. 11). In the case of MoTe\(_2\), where mainly the valence bands at \( K \) are doped, a description with 2D, quadratic, isotropic bands completely fails.

For n-type doping of all TMDs the DOS at the Fermi energy shows a quasi 2D behavior. It has steps when the conduction-band minimum at \( K \) or \( Q \) enters the bias window and is nearly constant in between. However, for larger electron doping the non-constant behavior increases. This is due to the stronger deviation of the spin-orbit-split conduction band at \( Q \) from a quadratic dispersion.

The in-plane conductivity \( \sigma_{xx}/\tau \) is another measure for the deviation from quadratic, isotropic bands in 2D. As can be seen in Eq. (16), for a perfect 2D electron gas the conductivity would be an increasing linear function of the doping-charge concentration \( n \). Most interestingly, the right-hand panel of Fig. 18 shows that \( \sigma_{xx}/\tau \) weakly differs from one TMD to the other and from the monolayer to the multilayer case. Only for the tungsten dichalcogenides the conductivity has a small non-linear component for n-type doping. This might be due to the stronger SOC of tungsten which leads also to larger deviation of the \( Q \) valley from a quadratic dispersion.

IV. CONCLUSIONS

In this work, we have calculated from ab initio the structural, electronic, and transport properties for
FIG. 18. DOS at the Fermi energy $E_F$ (left panel, $T = 0$ K) and in-plane conductivity $\sigma_{xx}/\tau$ (right panel, $T = 300$ K) as function of doping for the mono- (black, solid), bilayer (red, dashed), and trilayer (green, dash-dotted) of all investigated TMDs. Note also the different range of the ordinate for $\text{DOS}(E_F)$ in the case of WS$_2$ and WSe$_2$. Lines are guides for the eye.

The band structure and thus also the transport properties can be changed considerably under field-effect doping. We have shown that most TMDs behave similarly under hole doping while for electron doping they can be divided into two different classes: one in which the conductive channel has a width of approximately two layers for small doping (MoSe$_2$ and MoTe$_2$) and one in which the charge is localized within the first layer. This can be attributed to the relative position of the conduction-band minimum at K and Q in the multilayer TMDs. In the former class Q is lower than K and the doping charge first occupies the states in the Q valley. Since

mono-, bi-, and trilayer TMDs in field-effect configuration. We have first investigated the structural changes of the TMDs under field-effect doping. We found that the internal structure is only slightly changed but that it is nevertheless important to fully relax the system. We also showed that high electron doping can induce a phase transition from the 1H to the 1T' structure. In accordance with literature this transition can however only occur for electron doping larger than $n \leq -0.35 e/\text{unit cell}$. Therefore, we concentrated on smaller doping of the H polytype as it is the most stable structure found in nature.
these states have a large \( p_z \) contribution of chalcogen states, the hybridization between the layers is larger and the electrons are more delocalized. Additionally, for the tungsten dichalcogenides the difference between \( K \) and \( Q \) is smaller than for MoS\(_2\) and thus, as the electron doping is increased, the charge rapidly starts to occupy states at \( Q \). This leads to an increase of the width of the conductive channel to approximately two layers. For high electron doping only the \( Q \) valley is occupied in all investigated TMDs (also in the monolayer systems) and the width of the conductive channel is reduced to one layer.

Under hole doping most TMDs behave similarly: in the monolayer case first the valence-band maximum at \( K \) is occupied while in the multilayer case it is the \( \Gamma \) valley. This also leads to the delocalization of the doping charge over more layers as the states at \( \Gamma \) have large chalcogen \( p_z \) character. For large hole doping also in the monolayer case the doping at \( \Gamma \) is larger than those at \( K \). Only exception from this picture is MoTe\(_2\) in which the valence-band maximum for the undoped compound is always at \( K \) even in the multilayer case. Accordingly, the doping charge within the \( K \) valley is always larger than those at \( \Gamma \).

However, even if the thickness of the doping-charge distribution is approximately two layers for multilayer TMDs, the number of doped valleys can be comparable to the monolayer case. The main difference is between n-type and p-type doping: as the valley degeneracy for the conduction-band minimum at \( Q \) is \( g_q = 6 \), the total number of doped valleys can be as large as \( \nu = 16 \) while for hole doping the maximum is \( \nu = 8 \).

In the next part, we have seen that a Hall-effect measurement can often not directly be used in order to determine the charge-carrier concentration under the assumption of quadratic bands – the charge thus determined can be up to 1.5 times larger than the real doping charge within the sample. For MoTe\(_2\) the Hall coefficient \( R_{xy} \) even changes the sign due to the changing curvature of the valence band. Thus, an interpretation based on parabolic bands would lead to an incorrect sign of the charge of the carriers. Even if this can only be seen at low temperatures, the Hall-effect measurement still largely overestimates the doping charge concentration if one does not take into account the specific band structure. Only in the case of multilayer MoS\(_2\) the inverse Hall coefficient is directly proportional to the doping-charge concentration for a large range of electron and hole doping.

In this work, we have shown that it is important to correctly model an FET setup. The changes in the electronic and transport properties cannot be described with both the rigid doping and the uniform-background doping approach. We provide not only a full database of electronic structure of mono-, bi-, and trilayer dichalcogenides as a function of doping, but also a mapping between the doping charge and the Hall coefficient.

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FIG. 19. Band structure of mono-, bi-, trilayer, and bulk MoS$_2$. The arrow indicates the lowest-energy transition.
FIG. 20. Band structure of mono-, bi-, trilayer, and bulk MoSe$_2$. The arrow indicates the lowest-energy transition.
FIG. 21. Band structure of mono-, bi-, trilayer, and bulk MoTe$_2$. The arrow indicates the lowest-energy transition.
FIG. 22. Band structure of mono-, bi-, trilayer, and bulk WS$_2$. The arrow indicates the lowest-energy transition.
FIG. 23. Band structure of mono-, bi-, trilayer, and bulk WSe$_2$. The arrow indicates the lowest-energy transition.
Appendix B: Influence of structural relaxation in FET setup

FIG. 24. Comparison of the band structures of doped bilayer MoS$_2$ with and without relaxation. The doping is indicated in the labels. For the fixed structures we used the relaxed geometry of undoped bilayer MoS$_2$ and placed the system at approximately the same distance to the barrier potential as in the case of the fully relaxed system.
Appendix C: Influence of the asymmetric electric field in an FET

FIG. 25. Comparison of the band structures of doped monolayer MoSe$_2$ calculated with a compensating jellium background (homogeneous-background doping, “h.b.d.”) and the proper FET setup. The doping is indicated in the labels. All systems have been fully relaxed. The difference is negligible for a small doping of $n = \pm 0.02$ e/\text{unit cell}, but for a higher doping of $n = \pm 0.15$ e/\text{unit cell} one can see clear differences not only in the relative amount of doping in the different valleys but also in the curvature of the bands, i.e., their effective masses. Furthermore, it is difficult to model the system properly with a compensating jellium background for electron doping larger than $n = -0.15$ e/\text{unit cell} due to the interlayer states crossing the Fermi energy.
FIG. 26. Comparison of the band structures of doped trilayer MoSe$_2$ calculated with a compensating jellium background (homogeneous background doping, “h.b.d.”) and the proper FET setup. The doping is indicated in the labels. All systems have been fully relaxed. The difference is again small for a low doping of $n = \pm 0.02$ e/unit cell. However, in contrast to the monolayer case, in the FET setup other states are close to the Fermi energy which will change the Hall coefficient for finite temperature. For a higher doping of $n = \pm 0.15$ e/unit cell one can see clear differences not only in the relative amount of doping in the different valleys but also in the curvature of the bands, i.e., their effective masses. The differences are also larger for high hole doping as shown in the lower right panel.
Appendix D: Band structure of the doped TMDs

1. Molybdenum disulfide
FIG. 27. Band structure of monolayer MoS$_2$ for different doping as indicated in the labels.
FIG. 28. Band structure of monolayer MoS$_2$ for different doping as indicated in the labels.
FIG. 29. Band structure of monolayer MoS$_2$ for different doping as indicated in the labels.
FIG. 30. Band structure of bilayer MoS$_2$ for different doping as indicated in the labels.
FIG. 31. Band structure of bilayer MoS$_2$ for different doping as indicated in the labels.
FIG. 32. Band structure of bilayer MoS$_2$ for different doping as indicated in the labels.
FIG. 33. Band structure of trilayer MoS$_2$ for different doping as indicated in the labels.
FIG. 34. Band structure of trilayer MoS$_2$ for different doping as indicated in the labels.
2. Molybdenum diselenide
FIG. 35. Band structure of monolayer MoSe$_2$ for different doping as indicated in the labels.
FIG. 36. Band structure of monolayer MoSe$_2$ for different doping as indicated in the labels.
FIG. 37. Band structure of bilayer MoSe$_2$ for different doping as indicated in the labels.
FIG. 38. Band structure of bilayer MoSe$_2$ for different doping as indicated in the labels.
FIG. 39. Band structure of trilayer MoSe$_2$ for different doping as indicated in the labels.
FIG. 40. Band structure of trilayer MoSe$_2$ for different doping as indicated in the labels.
3. Molybdenum ditelluride
FIG. 41. Band structure of monolayer MoTe$_2$ for different doping as indicated in the labels.
FIG. 42. Band structure of monolayer MoTe$_2$ for different doping as indicated in the labels.
FIG. 43. Band structure of monolayer MoTe$_2$ for different doping as indicated in the labels.
FIG. 44. Band structure of monolayer MoTe$_2$ for different doping as indicated in the labels.
FIG. 45. Band structure of bilayer MoTe₂ for different doping as indicated in the labels.
FIG. 46. Band structure of bilayer MoTe$_2$ for different doping as indicated in the labels.
FIG. 47. Band structure of trilayer MoTe$_2$ for different doping as indicated in the labels.
FIG. 48. Band structure of trilayer MoTe$_2$ for different doping as indicated in the labels.
FIG. 49. Band structure of trilayer MoTe$_2$ for different doping as indicated in the labels.
FIG. 50. Band structure of trilayer MoTe$_2$ for different doping as indicated in the labels.
4. Tungsten disulfide
FIG. 51. Band structure of monolayer WS₂ for different doping as indicated in the labels.
FIG. 52. Band structure of monolayer WS$_2$ for different doping as indicated in the labels.
FIG. 53. Band structure of bilayer WS$_2$ for different doping as indicated in the labels.
FIG. 54. Band structure of bilayer WS$_2$ for different doping as indicated in the labels.
FIG. 55. Band structure of trilayer WS$_2$ for different doping as indicated in the labels.
FIG. 56. Band structure of trilayer WS$_2$ for different doping as indicated in the labels.
5. Tungsten diselenide
FIG. 57. Band structure of monolayer WSe$_2$ for different doping as indicated in the labels.
FIG. 58. Band structure of monolayer WSe$_2$ for different doping as indicated in the labels.
FIG. 59. Band structure of bilayer WSe$_2$ for different doping as indicated in the labels.
FIG. 60. Band structure of bilayer WSe$_2$ for different doping as indicated in the labels.
FIG. 61. Band structure of trilayer WSe$_2$ for different doping as indicated in the labels.
FIG. 62. Band structure of trilayer WSe$_2$ for different doping as indicated in the labels.
Appendix E: Hall measurements

![Graph showing the ratio of the inverse Hall coefficient $R_{xyz}^{-1}$ to the doping charge $n$ as a function of doping for all monolayer TMDs and temperatures $T = 0$ K and $T = 300$ K.]

FIG. 63. Ratio of the inverse Hall coefficient $R_{xyz}^{-1}$ to the doping charge $n$ as function of doping for all monolayer TMDs and temperatures $T = 0$ K and $T = 300$ K.
FIG. 64. Ratio of the inverse Hall coefficient $R_{xyz}^{-1}$ to the doping charge $n$ as function of doping for all bilayer TMDs and temperatures $T = 0$ K and $T = 300$ K.
FIG. 65. Ratio of the inverse Hall coefficient $R_{xyz}^{-1}$ to the doping charge $n$ as function of doping for all trilayer TMDs and temperatures $T = 0$ K and $T = 300$ K.