

Carrier Density Dependent Transport in Monolayer WS₂

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Abstract—The intrinsic transport properties of two-dimensional semiconducting transition metal dichalcogenides (TMDs) are dominated by electron-phonon interactions (EPI) within a multi-valley, spin-dependent band structure. The relative energy separations between these valleys are key parameters that determine the resulting transport characteristics. However, these separations are highly sensitive to external conditions, such as mechanical strain, doping, and applied fields. In this work, we present a first-principles approach to determine the valley separations as a function of the electron carrier density (N_s), using monolayer WS₂ as a representative material. In addition to the electronic band structure, we evaluate phonon dispersions and electron-phonon matrix elements at different carrier densities. Using an ensemble Monte Carlo (EMC) solver, velocity-field characteristics are extracted which exhibit a characteristic peak in drift velocity depending on the carrier density. We identify three distinct carrier-density-dependent mechanisms affecting the carrier transport; Pauli blocking, modifications of the valley profile, and phonon screening.

I. INTRODUCTION

Two-dimensional field-effect devices (2D-FET) promise a viable scaling path for logic devices in advanced technology nodes because of their intrinsic atomically thin channels, potential high carrier mobility, high gate control and, reduced surface effects (1–4). Two-dimensional semiconductors from the TMD family, such as WS₂ and MoS₂, are being extensively researched as channel materials for these devices (5). A comprehensive understanding of how the device environment influences the transport properties of these materials is essential for the further development of accurate theoretical models for *ab initio* carrier transport.

The conduction band of a TMD typically has its conduction band minima (CBM) at the K point, referred to as the K valley, as well as a secondary local minimum approximately halfway along the Γ – K direction, referred to as the Q valley (see Fig. 1). Owing to the large atomic numbers of the transition metal atoms, spin-orbit coupling cannot be neglected and leads to a splitting of the first conduction band, resulting in four distinct minima. The relative separation between these valleys, commonly referred to as the *valley profile*, determines which valleys contribute to carrier transport and which are accessible for scattering via the EPI. This valley profile can vary significantly across different TMDs (6, 7), and even within a single material depending on details of the *ab initio* calculations, such as applied strain, electrostatic doping, or the presence of external fields (8–10), as well as computational choices including pseudo-potentials

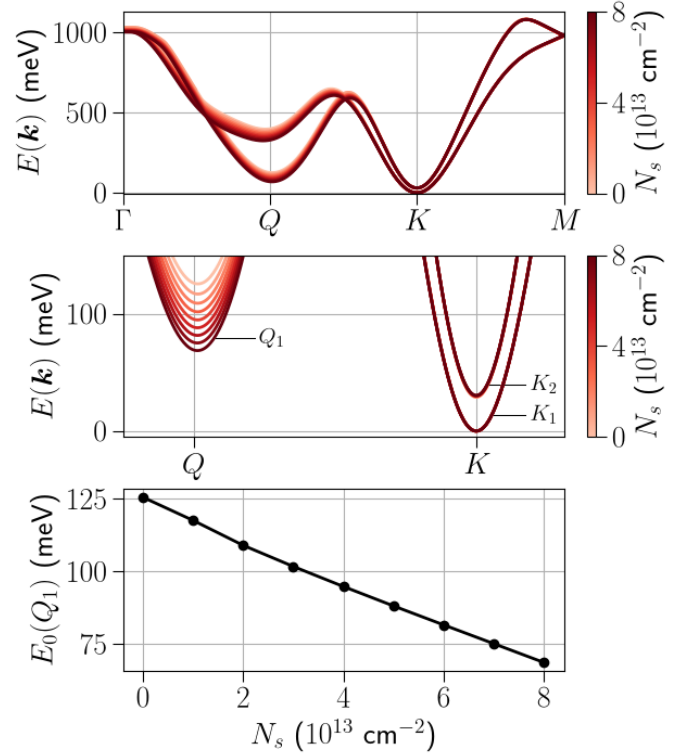


Fig. 1. **Top:** First conduction band of monolayer WS₂ relative to its CBM for various values of the carrier density N_s . The four valleys of the valley profile of a typical TMD are present, the K_1 valley as the CBM, the K_2 valley at around 29 meV above the CBM, the Q_1 valley at around 100 meV and, the Q_2 valley at around 370 meV, these values are specific to monolayer WS₂. **Middle:** Closer view of the top panel showing the changes in the Q_1 valley and, the lack of changes in the K_1 and K_2 valleys. **Bottom:** The valley offset of the Q_1 valley as a function of the carrier density.

and exchange-correlation functionals (11, 12). While variations arising from computational approximations reflect methodological differences, those induced by environmental effects are generally assumed physical and are observable experimentally (12, 13).

For a 2D-FET device to operate, doping of its 2D channel is essential. However, as chemical doping of TMDs is challenging, electrostatic doping is typically employed. This requires substantial gate biases, which generate strong transverse electric fields on the order of 10^6 V/cm and result in electron densities of a few 10^{13} cm^{-2} . Under these conditions, the Fermi level can vary from quasi-degenerate (aligned with the CBM) to highly degenerate regimes (several $k_b T$ inside the conduction band). The Fermi energy is taken to be

equivalent to the chemical potential. In this work, we investigate phonon-limited carrier transport, explicitly accounting for such environmental factors, including transverse electric fields and finite background charge densities.

II. METHODS

A. Ab-initio parameter extraction

Electronic band structures are obtained from density functional theory (DFT), while phonon dispersions and the corresponding scattering matrix elements are computed using density functional perturbation theory (DFPT), as implemented in QUANTUM ESPRESSO (14). Exchange–correlation effects are treated within the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA), and optimized norm-conserving Vanderbilt (ONCV) pseudopotentials are employed for all constituent elements. Brillouin–zone integrations are performed on a $12 \times 12 \times 1$ k–point grid and a $6 \times 6 \times 1$ q–point grid. Charge is introduced by setting a non-zero total electronic charge in the DFT calculations. Since the focus of this work lies in the conduction band applied charges are negative (excess electrons). Gaussian smearing is employed to aid electronic convergence. Maximally localized Wannier functions are constructed using WANNIER90 (15) and are used to interpolate the electronic band structure and electron–phonon matrix elements. Bandstructure and phonon dispersions are later interpolated with the PERTURBO (16) software package on a $1000 \times 1000 \times 1$ grid. Electron–phonon matrix elements are interpolated on a triangular 12×12 mesh (see ref. (17)). Since WS₂ is significantly affected by spin–orbit coupling, it is included in the calculations. The dispersion of the valley profile $E_n(\mathbf{k})$ is approximated by the non–parabolic Kane dispersion, where $\varepsilon_n(\mathbf{k}) = E_n(\mathbf{k}) - E_{n0}$, the valley energy relative to the valley offset,

$$\varepsilon_n(\mathbf{k}) (1 + \alpha_n \varepsilon_n(\mathbf{k})) = \frac{\hbar^2}{2} \left(\frac{k_l^2}{m_{nl}} + \frac{k_t^2}{m_{nt}} \right), \quad (1)$$

here n labels the specific valley, m_{nl}, m_{nt} are the effective masses in the longitudinal and transversal directions respectively and α_n is the non–paraboliocity factor. The energy resolved density of states (DoS) of this dispersion is given by

$$\rho_n(E) = g_n \frac{\sqrt{m_{nl}m_{nt}}}{2\pi\hbar^2} (1 + 2\alpha_n(E - E_{n0})), \quad (2)$$

where g_n is the total degeneracy of the valley. We obtained these parameters by fitting the bottom of the DFT bandstructure data, interpolated on a fine k–grid, to Eq. 1. The carrier density, can be computed by taking the integral over the DoS and the distribution function f for all valleys

$$N_s = \sum_n \int_{E_{n0}}^{+\infty} f(E) \rho_n(E) dE, \quad (3)$$

if we assume $f(E)$ to be the Fermi–Dirac distribution function we get,

$$N_s = \frac{k_b T}{2\pi\hbar^2} \sum_n g_n \sqrt{m_{nl}m_{nt}} \left((1 + 2\alpha_n E_{n0}) \ln(1 + e^{\eta_n}) + 2\alpha_n k_b T \mathcal{F}_1(\eta_n) \right) \quad (4)$$

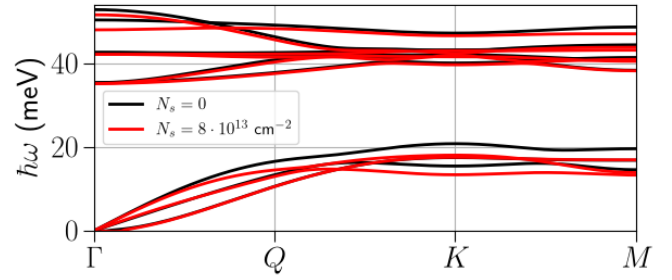


Fig. 2. Phonon dispersion of monolayer WS₂ along a high symmetry path, computed with DFPT for an electrically neutral background and, a strong negatively charged background.

with $\eta_n = (E_f - E_{n0})/k_b T$, the reduced Fermi energy in thermal units and $\mathcal{F}_1$ the complete Fermi–Dirac integral of first order. Since the valley profile is dependent on the density Eq. 4 needs to be inverted to get the correct Fermi energy for a given N_s . The carrier densities studied in this work range up to $8 \cdot 10^{13} \text{ cm}^{-2}$, corresponding to a Fermi energy of 122.7 meV above the CBM.

B. Monte Carlo transport solver

The transport results in this work are obtained using an in–house developed ensemble Monte Carlo (EMC) solver. The incorporation of first–principles material properties such as the band structure, phonon dispersions, and scattering rates into this solver was presented in the SISPAD 2025 proceedings (Ref. (17)). The results reported here are benchmarked against the computationally more demanding approach based on full–band, full–phonon, and full matrix elements, as described in Ref. (17).

III. RESULTS

A transverse electric field $F_\perp$ was included in the first–principles calculations for monolayer WS₂, with field strengths ranging from 0 to 10^7 V/cm . The inclusion of this field does not lead to any significant modifications of the electronic structure, as a field applied in this direction does not break the symmetries of the system (18), in agreement with previous observations. In the following subsections the changes due to the inclusion of a non–zero background charge are discussed.

A. Bandstructure

The band structure for several values of the carrier density N_s is shown in Fig. 1. Near the CBM the effect of increasing N_s is negligible. However, the separation between the Q and K valleys is lowered by charge while the valley shape (the effective mass and non–paraboliocity) are unaffected. The influence of the carrier density can therefore be described primarily as a modification of the valley offset E_0 of the Q_1 and Q_2 valleys, of which the former is expected to have a noticeable impact on transport having an almost linear decrease with increasing density of $7.1 \text{ meV}/(10^{13} \text{ cm}^{-2})$.

B. Phonon dispersions and scatter rates

The phonon dispersion under neutral conditions and at high carrier density are shown in Fig. 2. The most pronounced modification is the softening of the acoustic modes near the

Brillouin-zone edge (along the K - M direction). Interaction with these zone-edge modes constitute the dominant scattering mechanism for $K \rightarrow Q$ intervalley transitions, and their softening is therefore expected to alter the corresponding transition rates with increasing carrier density. To perform a rigorous analysis of the scattering rates, we extract the full EPI matrix elements and compute the full-band scattering rates for each carrier density following the methodology of Ref. (17). In general, the scattering rates are proportional to an effective coupling strength V , which depends on the phonon mode ν , the electronic transition nm , and the carrier density. For elastic scattering with acoustic phonons near the zone centre, the scattering rate can be approximated as

$$\frac{1}{\tau_{n\nu}(\mathbf{k})} \approx V_{n\nu} \rho_n(E_n(\mathbf{k})). \quad (5)$$

For optical modes, as well as acoustic modes near the zone edge with phonon energy $\hbar\omega_\nu$, scattering from valley n to valley m is given by

$$\frac{1}{\tau_{nm\nu}(\mathbf{k})} \approx V_{nm\nu} \left(N_\nu + \frac{1}{2} \pm \frac{1}{2} \right) \rho_m(E_n(\mathbf{k}) \mp \hbar\omega_\nu), \quad (6)$$

where ρ_m denotes the density of states of the final valley (Eq. 2), $\pm$ for emission/absorption of a phonon mode respectively and, $N_\nu = (\exp(\hbar\omega_\nu/k_bT) - 1)^{-1}$ is the occupation of phonon mode ν . The phonon softening discussed above leads to higher phonon occupation numbers N_ν , which enhances the associated scattering rates. At the same time, the effective scattering potential V is reduced due to electrostatic screening of the EPI. The overall behaviour of the scattering rates with carrier density is therefore governed by the competition between phonon softening, which increases scattering, and screening, which suppresses it.

Figure 3 shows the ensemble-averaged scattering rate, assuming Fermi-Dirac statistics, as a function of the carrier density N_s ,

$$\langle \tau_n^{-1} \rangle = \frac{\int_{E_{n0}}^{+\infty} f(E) \rho_n(E) \sum_{m\nu} \tau_{nm\nu}^{-1} dE}{\int_{E_{n0}}^{+\infty} f(E) \rho_n(E) dE}. \quad (7)$$

The acoustic scattering rate increases, as expected; however, this increase cannot be attributed solely to the change in phonon energies alone. The relative shift of the valleys, as described in Fig. 1, allows for a larger number of electronic states to participate in intervalley transitions at a given carrier energy. In particular, $K \rightarrow Q_1$ transitions become accessible at energies closer to the CBM making the ensemble scatter rate increase with N_s .

C. Mean free path

The mean free path ℓ_n is a key indicator of how a given valley n contributes to transport. It is calculated as

$$\ell_n(\mathbf{k}) = \frac{v_n(\mathbf{k})}{\sum_{m\nu} \tau_{nm\nu}^{-1}(\mathbf{k})}, \quad (8)$$

where $v_n(\mathbf{k}) = \hbar^{-1} \nabla_{\mathbf{k}} E_n(\mathbf{k})$, the group velocity. Taking the ensemble average of Eq. 8 allows for a comparison across different carrier densities, shown in Fig. 4. The mean free path is

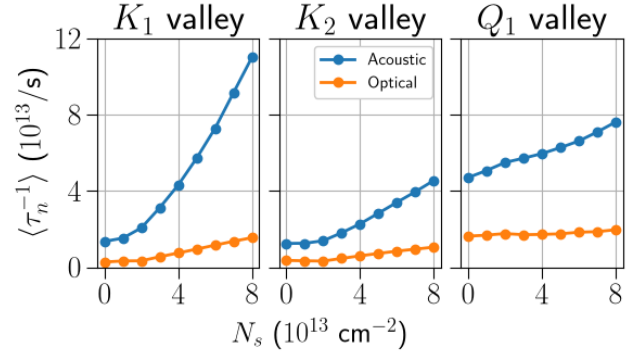


Fig. 3. Ensemble average of the scatter rate in the three lowest valleys (see Eq. 7). Sum of all three acoustic modes in blue and, sum of all six optical ones in orange.

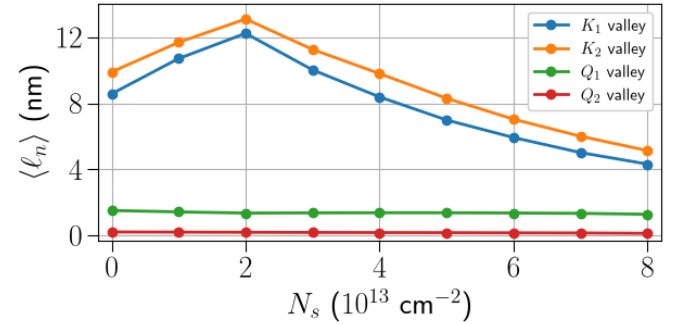


Fig. 4. Ensemble average mean free path of the four valleys in the first conduction band of monolayer WS_2 as a function of N_s .

substantially smaller in the Q valleys. Consequently, when these valleys contribute significantly to transport, quantities such as drift velocity and mobility are reduced. The K valleys initially exhibit an increase in the mean free path, primarily due to changes in the distribution function and screening of the EPI. As N_s increases, lower-energy states in these valleys become more occupied, leading to a higher relative occupation of states with larger group velocities and, hence, a larger mean free path. At higher carrier densities, however, the valley shift discussed in Sec. III-A brings these high-energy states into a regime where scattering into the Q_1 valley via absorption becomes possible, increasing the total scattering rate and thereby reducing the mean free path.

D. Velocity field curves

The phonon-limited velocity-field characteristics of electron transport in monolayer WS_2 , obtained from EMC simulations, are shown in Fig. 5. Each velocity-field curve exhibits a linear response of the drift velocity to the applied field for low fields ($F \sim 10^3$ V/cm), which enables the extraction of the carrier mobility via $v_d = \mu F$. In practice, to suppress statistical noise inherent to the EMC method, we determine the mobility through a least-squares procedure,

$$\mu = \frac{\sum_j v_j F_j}{\sum_j F_j^2}, \quad (9)$$

where the summation is restricted to the linear response regime. This regime is characterized by a constant valley occupation, *i.e.*, the relative carrier population in each valley does not vary

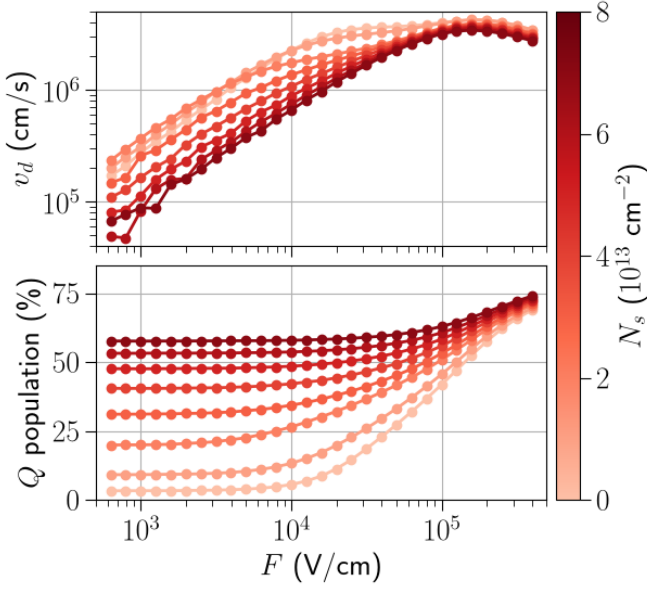


Fig. 5. **Top:** Velocity field curves of free-standing monolayer WS₂ for various carrier densities on a log-log plot. **Bottom:** The population of the *Q* valley (*Q*₁ + *Q*₂) as a function of transport field *F* and carrier density *N_s*.

with the applied field. At higher fields ($F \sim 10^4$ V/cm), this behaviour changes; the *Q* valley occupation increases, reducing the rate of increase in the drift velocity due to the substantially lower mean free path in these valleys (see Fig. 4). At even higher fields ($F \sim 10^5$ V/cm), the velocity-field curves exhibit a pronounced peak, indicating the onset of *negative differential mobility* characteristic of transport in multi-valley semiconductors.

The inclusion of carrier density can be understood as the combined effect of three distinct mechanisms. First, with increasing carrier density, electronic states near the CBM in the *K* valleys become increasingly occupied. As a consequence, scattering into these states is suppressed by the factor $(1-f(E))$, effectively driving the electron population toward higher-energy regions of the band structure. This effect is commonly referred to as *Pauli blocking*. Second, the band structure modifications discussed in Sec. III-A. Third, the phonon softening and phonon screening discussed in Sec. III-B modify the EPI and, consequently, alter the transport behaviour of the carriers. To better understand the sensitivity of the mobility to these mechanisms, we carried out simulations in which we start from the neutral case and vary only one single aspect of the system. Figure 6 shows the change in mobility resulting from each of the three mechanisms individually, as well as the total mobility of the real material extracted from the data in Fig. 5. As expected, the modifications to the valley profile reduce the mobility due to the increased occupation of the *Q* valleys, enabled by the reduced energy separation between the *K* and *Q* valleys; this trend is also reflected in Fig. 5, where the *Q* valley population increases at a given field with carrier density. Pauli blocking initially leads to an increase in mobility, as scattering to states near the CBM are suppressed and higher-energy states with larger group velocities become

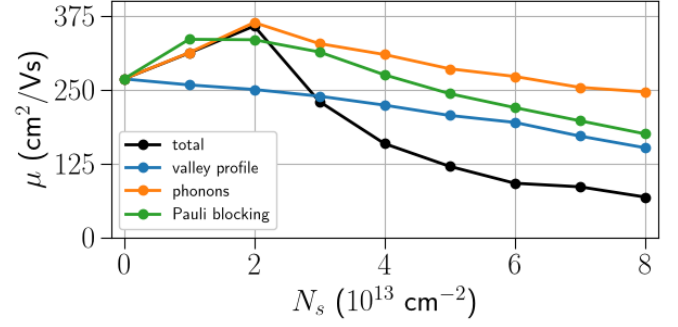


Fig. 6. Low-field mobility extracted from the linear response region of velocity-field curves using Eq. 9 as a function of *N_s*. In black the carrier density dependent mobility of phonon-limited transport in monolayer WS₂, in blue if only the valley profile would change and all other properties would be that of the neutral material, in orange if only phonon screening and softening would take place and, in green if only the Fermi level would change.

more occupied; however, at higher sheet densities mobility is reduced, as these states become increasingly susceptible to intervalley scattering, effectively pushing carriers toward regions with a lower mean free path. The screening and softening of the phonon modes initially increase the mobility due to a reduction in the EPI coupling strength. However, this reduction is partially counteracted by the softening of the phonon modes themselves, which leads to higher phonon occupation numbers (see Eq. 6). The total mobility is determined by the interplay of these three mechanisms and shows a peak value of $358 \text{ cm}^2/\text{Vs}$ at $N_s = 2 \cdot 10^{13} \text{ cm}^{-2}$.

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