The impact of valley profile on the mobility and Kerr rotation of transition metal dichalcogenides

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Abstract

The transport and optical properties of semiconducting transition metal dichalcogenides around room temperature are dictated by electron–phonon scattering mechanisms within a complex, spin-textured and multi-valley electronic landscape. The relative positions of the valleys are critical, yet they are sensitive to external parameters and very difficult to determine directly. We propose a first-principles model as a function of valley positions to calculate carrier mobility and Kerr rotation angles, and apply it to MoS\textsubscript{2}, WS\textsubscript{2}, MoSe\textsubscript{2}, and WSe\textsubscript{2}. The model brings valuable insights, as well as quantitative predictions of macroscopic properties for a wide range of carrier density. The doping-dependent mobility displays a characteristic peak, the height depending on the position of the valleys. In parallel, the Kerr rotation signal is enhanced when same spin-valleys are aligned, and quenched when opposite spin-valleys are populated. We provide guidelines to optimize and correlate these quantities with respect to experimental parameters, as well as the theoretical support for in situ characterization of the valley positions.

1. Introduction

Semiconducting transition-metal dichalcogenides (TMDs) hold center stage in the flatland\cite{1}. They are among the most intensely studied 2D materials, along with graphene and boron nitride. TMDs display extremely rich physics that have been explored via their optical\cite{2–7} and charge/spin transport properties\cite{8–10}, most often as a function of electrostatic doping\cite{11–13}. For example, one observes: high mobility\cite{14–19}; ambipolar behavior\cite{20}; insulator-metal-superconductor transitions\cite{21–25}; the valley Hall effect\cite{26}; and a variety of bright and spin-orbital-dark excitons\cite{27,28}. This rich physics can be linked to a multivalley band structure with a polarized spin texture coming from strong spin-orbit interactions\cite{2,29}. The strong and sometimes unexplained variations of macroscopic observables as a function of external parameters (strain, doping...) reflect the scattering of electrons within this complex electronic structure. The intrinsic scattering coming from electron–phonon interactions (EPIs) is especially relevant at room temperature.

The relative position of the different valleys (at different momenta and with different spins), which we call ‘valley profile’ hereafter, dictates which valleys are occupied and/or available for scattering at different doping levels or optical excitation energies. The valley profile naturally emerges as a key parameter in the opto-electronic properties of TMDs\cite{19,30–33}. Our understanding of TMD physics is then challenged by the strong variations of this parameter across different TMDs, or even the same TMDs in different experimental or simulation setups. For the latter, one notes the variability of valley profile in ab initio works\cite{19,32–41}, highlighting a sensitivity to many factors including the exact structure, the pseudo-potentials used, the exchange correlation density functional, the inclusion and type...
of van der Waals correction, the level of theory, etc. This variability is physical, and also observed in experiments: while measurements of the conduction band profile are difficult and rare [42], values for the valence band can be found more easily [30, 31, 43–52], mostly using angle-resolved photo-emission spectroscopy. Based on variations of the relative valley positions on the order of 100 meV for the same material, one can infer that the valley profile depends on the environment of the 2D material and the details of the setup, including dielectric, strain, interfacial interactions with the encapsulant, or defects. A telling example of this sensitivity to external parameters is the dependency of the valley profile on the geometric thickness of single layers of TMDs. A recent work [19] has shown that a variation of the thickness of 1% leads to a change in the relative position of the valleys of ≈100 meV. Since the impact of thickness is very clear (in simulations and most likely experimentally) and probably dominant, it will be used in the following as a proxy for all potential factors affecting valley profile.

Gate-controlled electrostatic doping is ubiquitous in transport setups and devices based on 2D materials, and it is present in virtually all the experimental references cited here. The latest electrolyte gating technologies [12, 13] go up to densities of a few 10¹⁵ cm⁻², enabling significant variations of the Fermi level (taken to be equivalent to the chemical potential throughout this work). Similarly, the area density of excited electrons-hole pairs pumped in the material is a natural tuning parameter in optical experiments. The quantities are different but loosely and collectively referred to as doping, and play a very important role here as they allow us to explore the valleys.

In order to understand and control the opto-electronic properties of TMDs, it is crucial to study the impact of valley profile and doping on electron–phonon scattering. The first consequence is on the electronic states which can be filled as a function of doping, and those that remain available for scattering. Another very important aspect is the impact on free-carrier screening of the EPIs. In addition to the usual dependency of free-carrier screening on the density of states and the shape of the Fermi surface, peculiar multi-valley screening effects have been discovered for certain phonon modes [33]. The role of valley profile has been pointed out in recent experiments to explain the variation of transport measurements versus doping [24, 53, 54] or strain in TMDs [55]. This was based on an earlier theoretical study of mobility versus in-plane strain [56]. However, EPIs were simply modeled with deformation potentials and were assumed to be unscreened, which is incorrect for intravalley scattering, as we will see.

In this work we propose an ab initio model of electron–phonon scattering to predict transport (carrier mobility) and optical properties (Kerr signal) at room temperature, with doping and valley profile as parameters. EPIs are calculated within density functional perturbation theory (DFPT). For transport, we focus notably on modeling the impactful variation of the screening of intravalley EPIs. Mobility is simulated within the full energy- and momentum-dependent Boltzmann equation, which is solved iteratively. We arrive at a unified understanding of transport for both electrons and holes in all semiconducting TMDs, and show how the mobility peaks as a function of doping, when the degenerate regime is reached. When the secondary valleys are close to the band edge (low Q valley or high Γ valley), the mobility is decreased. We expect the transport simulations to be quantitatively accurate for clean devices at room temperature where transport is limited by phonons. The results thus provide clear guidelines to the experimental community to optimize transport, and they suggest the possibility to reverse engineer, and characterize the valley profile from doping-dependent mobility measurements. The Kerr signal is extracted from the solution of the Bethe–Salpeter equation (BSE) [57], and we focus on the carrier population dynamics driven by intervalley EPIs, based on results from previous works on the impact and characteristic time scales of the EPI in temperature-dependent scattering mechanisms on TMDs [57, 58].

We show that the Kerr signal is extremely sensitive to the valley energy profile of the conduction bands while variations are expected to be less important for the valence band. This sensitivity depends on the individual TMD through differences in spin–orbit coupling strength, the thickness of the monolayer, and the different energy alignment of the valleys. Our results show how Kerr can also be used as an indirect measurement of valley energy alignment and changes in the TMD layer thickness, by comparing the enhancement or quenching of the signal.

2. Results

The typical valley and spin structure of semiconducting TMDs is represented in figure 1, using WS₂ at the density-functional theory (DFT) level as an example. The valley profile refers to the energy difference between the edges of valleys at different momenta, ∆KQ and ∆KΓ for the conduction and valence bands. Those parameters are shown in figure 1, along with their variation as a function of the geometric thickness of a monolayer (for WS₂, other TMDs in supplementary information S1). Within DFT, selenium compounds generally display small ∆KQ < 100 meV and very large ∆KΓ > 250 meV, while sulfur compounds display moderate ∆KQ and ∆KΓ (100–200 meV). The thickness variations in each TMD are chosen such that ∆KQ roughly covers the 0–200 meV range, while staying within a maximum thickness variation of 2%. Note that the variation in energy is
on the order of 5 meV per unit-cell for a 1% thickness variation. Such a thickness variation is experimentally accessible with pressure [59, 60], and we expect it to be reached unintentionally in many devices. For WS$_2$, WSe$_2$, and MoSe$_2$ this is not sufficient to bring the ΔK$\Gamma$ under 150 meV, making the exploration of the Γ valley by holes unlikely. Spins are mostly oriented in the out of plane direction, with the relative polarities (spin up or down) of the valleys dictated by time reversal symmetry. The spin–orbit splitting is relatively large for the Q valleys and the K valleys of the valence band, while it is weaker for the conduction K valleys, and vanishes for the Γ valley. Spin splitting is overall stronger in WX$_2$ than in MoX$_2$. The spin structure is fully accounted for, but it is not considered as a parameter, and the spin-splitting energies are kept at the DFT values.

Mobility and Kerr rotation signal are simulated as a function of valley profile and carrier density. For transport calculations, the valley profile of both the conduction and valence band are modified. The variations in the screening of intravalley EPIs are modeled as described in section 3. In particular, we account for standard free carrier screening and propose a simple model in the context of out-of-phase multi-valley deformation potentials to account for the unusual enhancement of EPIs with double occupation [33]. In G$_0$W$_0$ + BSE Kerr simulations, given the cost of the calculations and, as noted above, the fact that the Γ valley is in general too low to be explored by excited carriers, we focus on variations of the conduction valley profile. We use different combinations of temperatures and chemical potentials to create populations of excited electrons and holes. The holes will concentrate near the K and Γ valleys, while the electrons will be concentrated in the K$^+$ and Q$^+$ or the K$^-$ and Q$^-$ valleys. The goal is to simulate an intermediate state in a pump-and-probe experiment, where the electrons have had time to scatter (conserving spin) from the K$^+$ (K$^-$) to the Q$^+$ (Q$^-$) valley, but have not yet had time to scatter to valleys with opposite spin, or to recombine. No phonon contributions to the dielectric screening are taken into account, which is kept purely at the electronic level. Previous work has shown that this is enough to capture almost all essential features in the Kerr signal [57, 61]: the main effect of the EPI is in the intervalley scattering, where it plays a dominant role in the process of balancing the opposite spin carrier populations.

We now discuss the results for transport and Kerr rotation: computations and models are detailed in section 3 below.

2.1. Transport as a function of electrostatic doping and valley profile

In agreement with existing works [19, 32–38, 40], the phonon-limited mobility is found to be dominated by (a) intravalley scattering with transverse and longitudinal acoustic (TA, LA), longitudinal optical (LO), and the out-of-plane homopolar (A1) phonons, and (b) intervalley scattering with zone boundary acoustic phonons. Doping and valley profile generally impact scattering by modifying which states are involved. This is the main effect involved in intervalley scattering. For intravalley scattering, an additional effect comes from free-carrier screening, via two mechanisms. The first, acting on the LO and TA modes, is the standard free-carrier screening which always attenuates electron–phonon couplings as doping increases. The second is a more peculiar

Figure 1. (Left) Electron and hole spin-valley texture of semiconducting TMDs, for the representative case of WS$_2$. Orange and blue colors indicate the spin texture: up or down in the out of plane direction. Electron valleys (top of figure 1) are situated at the corner of the hexagonal Brillouin zone (K valleys), or approximately midway between zone center and the corners (Q valleys). Hole valleys (bottom of figure 1) are situated at the corners (K valleys) and at zone center (Γ valleys). Every state in the BZ is represented exactly once, such that only two K valleys are represented, the other four being equivalent by a translation following the reciprocal vectors. Each valley is spin-split due to the spin–orbit (SO) interaction. Note that the gap has been reduced in this visualization. (Right) ΔKQ (left) and ΔKΓ (right) as a function of thickness variation Δt and carrier density (color scale).
Figure 2. Room-temperature mobility as a function of electron or hole density (x-axis) and valley profile (color) for WS₂ and MoS₂. Each curve corresponds to a different thickness with a different (doping-dependent) valley profile. The thickness variations are indicated in the order consistent with the color bar. The single point at \( n_p = 10^{11} \text{ cm}^{-2} \) is the mobility in the low-doping limit, computed with the EPIs of the neutral material with the relaxed structure.

multi-valley mechanism, that can actually enhance the coupling with LA and A1 modes at large doping, when K and Q (or Γ') are both occupied [33, 62, 63]. While some works have considered standard screening in the literature [64–66], the multivalley mechanism was only recently understood qualitatively for the A1 mode [33] and has not yet been accounted for in mobility simulations. Here, it is modeled quantitatively (see section 3) and discovered to govern the coupling to the LA mode as well. This comes from the fact that the LA displacement pattern involves an out-of-plane A1-like component. This multivalley mechanism turns out to be extremely important to obtain accurate mobility as a function of doping and valley-profile. Figure 2 shows the mobility of electron and hole-doped WS₂ and MoS₂ as a function of carrier density for different valley profiles. At low doping, only the K valley is occupied and intravalley scattering dictates the behavior of the mobility. The mobility increases as a function of doping, and reaches a peak around the degenerate regime, i.e. when the Fermi level hits the band edge. This behavior was noted previously in TMDs [56, 64], and is expected to be general for materials dominated by screened interactions. The presence of a mobility peak as a function of doping points to the fact that the enhancement of the conductivity \( \sigma \) due to screening is eventually overruled by the inverse dependency of mobility on carrier density, \( \mu = \sigma/n \). The position of the peak, however, is related to the details of scattering and the contribution from unscreened couplings as well. Consequently, our findings significantly differ from previous theoretical models of doping-dependent mobility in TMDs [56, 64, 66], in which EPIs models were simplified with respect to the DFPT calculations performed here. In particular, the effects of valley-profile on the screening (especially via the multivalley screening mechanism) were not accounted for. The peak flattens when \( \Delta KQ \) or \( \Delta K \Gamma \) is reduced. Indeed, the reduction results in a larger proportion of intervalley scattering, which is associated with rather strong electron–phonon couplings which are not screened by free carriers (see SI). In addition, multi-valley occupation causes the screening of the A1 and LA phonons to vanish (see details of the physical mechanism in section 3). As a result, the screening-induced peak gradually disappears, and the mobility is overall reduced. The strong dependency on valley profile is reduced but remains in the low-doping limit, which could explain some of the variations in the low-doping mobility results found in the literature [34–38, 40, 67]. Note that a striking electron–hole symmetry appears concerning the general behavior of mobility in MoS₂. The main difference is that the spin splitting of the K valley is stronger in the valence band, leading to generally higher mobility, as the intervalley K–K′ scattering involves improbable spin-flip transitions. Otherwise,
the Γ and Q valleys play a similar role, with similar impact because the corresponding electron–phonon couplings and density of states are roughly equivalent (accounting for degeneracies). The electron–hole symmetry is not as visible for other TMDs, because ΔK′ stays relatively large within the imposed limit of 2% thickness variation. We thus arrive at a unified understanding, for electron- and hole-doped TMDs, of the role of phonon scattering in mobility trends versus doping and valley profile.

These results bring several insights and opportunities to support the experimental community. First, we provide the mobility for the entire range of experimentally accessible doping, when most previous ab initio studies cover only the low doping limit [35–38]. Given the strong variations of mobility as a function of doping, we expect this to significantly improve comparisons of theoretical and experimental data. In addition, we use a more accurate DFPT-based model of the EPIs compared to the few previous studies considering doping dependency [56, 64] (see section 3 and SI), and quantitative comparison with experiment is meaningful. Second, we see that a simple rule of thumb to optimize the mobility of TMDs is to work with a carrier density around 8 × 10¹² cm⁻². More precise values for the optimal densities can be extracted from the plots. Third, considering the valley profile as a variable parameter enables its characterization in situ, by fitting to doping-dependent mobility measurements. Finally, we propose the geometric thickness as an experimental knob to increase the mobility. Unfortunately, the trend is opposite for electrons and holes: one should decrease or increase the thickness to enhance the electron or hole mobility, respectively (see figure 1).

2.2. Kerr as a function of excited carrier density and valley profile

The Kerr signal measures the angle between the polarization of incident and reflected electromagnetic fields, which is proportional to the surface magnetization density. This is often produced in a pump-and-probe setup with a circularly polarized pump which injects angular momentum and magnetization, which is later measured by a linearly polarized probe. TMDs have a very specific band structure [68], with spin-valley but also orbital-valley locking: the K⁺ and K⁻ valleys host conduction bands with opposite spin, and roughly 0 orbital momentum (dₓ²–y² orbitals). The corresponding valence bands have the same spin, but an orbital momentum of ±2 (dₓ²–y² and dₓy orbitals). Finally, the valence and conduction bands have opposite “pseudospin” associated to the A and B sublattices of the honeycomb lattice, occupied by the transition metal and the chalcogens. In total, the circularly polarized pump creates a population of spin-polarized electrons and holes (net spin 0) and a magnetization stored in the orbital and pseudospin degrees of freedom [69]. Due to the spin-valley coupling in TMDs, the spectroscopy can be used to track the populations in each valley, since the Kerr angle will only be finite if the K⁺ and K⁻ valley populations are different. It has been shown in the past that the EPI plays a fundamental role in balancing the populations between the valleys [57, 58, 61]. The direct transition between K⁺ and K⁻ through EPI scattering is forbidden due to symmetry which imposes spin conservation at K, so the excited carriers start by spreading through the neighborhoods of K⁺ or K⁻ in the BZ. States at lower symmetry points outside K⁺/K⁻ are not pure spinors and so electrons and holes are then allowed to scatter into valleys of opposite spin and magnetic orbital momentum. Nevertheless, scattering to the Q valley with the same spin polarization is still the most favorable process, especially at higher temperatures when ΔKQ ~ k_BT. This is indeed the process that explains the sign inversion of the Kerr signal with increasing temperature in MoSe₂ [58].

Results are shown in figure 3 for two materials, WS₂ and MoS₂, with a total of 300 excited configurations per material, one for each pair (µₑ, T). The data for WSe₂ and MoSe₂ can be found in the SI. These
occupied configurations are chosen as a thermalized pseudo-equilibrium, reflecting the dominant EPI scattering channels described above. The goal is to arrive at a qualitative relation between the Kerr rotation angle \( \theta_{\text{Kerr}} \) and the density of excited electrons for each material, depending on the splitting \( \Delta KQ \). Once the full \( \theta_{\text{Kerr}}(\omega) \) is obtained (see the SI for examples of these figures), we select the amplitude at the energy corresponding to each TMD’s A exciton, determined from a BSE absorption calculation, as is often done in experiments. For the lowest value of electronic density the highest Kerr amplitude is obtained for the case where \( \Delta KQ = 0 \); when the K and Q valleys are aligned in energy and it is easy to populate both bands with electrons.

Since both \( K^+ / K^- \) and \( Q^+ / Q^- \) valleys have parallel magnetization contributions, the electron populations will reinforce the Kerr amplitude. As the \( \Delta KQ \) energy splitting increases, it becomes harder to populate both \( K^\pm \) and \( Q^\pm \). If the \( \Delta KQ \) splitting is smaller than that produced by SOC, then it is still possible to change \( (\mu_e, T_e) \) so that the lowest conduction states in \( Q^\pm \) are populated. If this is not possible, then an increase in the electronic density leads to electrons being placed in the next conduction band at K, which is strongly polarized in the opposite spin, but the same orbital contribution, and thus creates an opposite magnetization. In the meanwhile the density of holes must increase to enforce charge neutrality, and this contributes to reverse the net Kerr amplitude sign. This also serves to explain why there is a significant difference in behavior between the W and the Mo based TMDs: the former have the largest values of energy splitting due to SOC, so it is easier to reach the Q valley by changing \( (\mu_e, T_e) \). The latter have lower SOC-induced energy splittings, and increasing the electronic density by changing \( (\mu_e, T_e) \) will quickly place electrons in the second band in both K and Q valleys. This also means that for Mo-based TMDs it is easier to reach higher densities of excited electrons, especially when \( \Delta KQ = 0 \), as it is shown at the bottom of figure 3.

In figure 4 we show how the Kerr amplitude evolves as a function of the splitting \( \Delta \) for each material for the lowest electron density (in the order of \( 10^{11} \) cm\(^{-2} \)). Since each value of \( \Delta KQ \) corresponds to different levels of \( \Delta t \), we do not represent them in the data and the colors correspond to different materials. Note that the correspondence between \( \Delta KQ \) and \( \Delta t \) can depend strongly on the pseudo potential used during the DFT calculations. The data represented summarizes the trend in figure 3: WSe\(_2\) will have the largest Kerr amplitude, followed by WS\(_2\), MoSe\(_2\), and MoS\(_2\). As the \( \Delta KQ \) splitting increases for all materials, the Kerr amplitude decreases. All these results show that in certain regimes the Kerr amplitude should be sensitive enough to measure the value of \( \Delta KQ \) in a TMD, even after a change of the thickness due to the presence of a substrate or encapsulating material.

3. Methods

All data and code necessary to generate the results are available as a Materials Cloud archive [70].

3.1. Mobility

In this section, we describe the process to account for the main effects of valley profile and doping on EPIs and phonon-limited transport. One could in principle simulate transport at many dopings and thicknesses, and relate the results to valley profile variations, as we have done in the past [19]. However, too many full-system simulations would be involved, which is computationally prohibitive at this point. A full analytical model, on the other hand, would require accounting for complex angular dependencies coming from wavefunction brackets and interference between different contributions to the electron–phonon coupling [35]. Instead, we aim at accounting for the variations in doping and valley profile by correcting the results of one reference \textit{ab initio} calculation. We start from high-accuracy simulations of the relaxed TMD monolayer doped at \( n/p = 5 \times 10^{12} \) cm\(^{-2} \) with either electrons or holes, hereafter referred to as the reference system. We use the Quantum ESPRESSO suite [71, 72] with 2D boundary conditions and gate electrostatics [73]. We then change the doping \( n \) (or \( p \)) and the valley profile \( \Delta KQ \) (or \( \Delta K^\Gamma \)) as a post-processing step before we solve the Boltzmann transport equation (BTE) to obtain the mobility. The BTE includes the full momentum and energy dependency of the scattering and is solved iteratively. The general process of computing phonon-limited transport in the reference system is described extensively in [32], with an update...
on the projection of the velocities (as mentioned in [74]), and the addition of spin–orbit coupling (as was already the case in [19]). For this work we brought a significant additional improvement that is the use of a non-uniform k-point grid, as shown in figure 5, to capture the Fermi surface effects more accurately. Although quite important, this is rather technical and we discuss it further in the SI along with other computational details.

We now discuss the main methodological development for the transport part of this work: a model which includes valley profile and doping, and the associated corrections to electron–phonon scattering. Starting from a fine sampling of the band structure (120 × 120 k-points grid) calculated in the neutral material, an energy shift is applied to a given valley (e.g. Q) using our post-processing framework that groups the states into valleys \((e.g. Q)\) using our post-processing framework that is modeled in the following. We will work within the adiabatic approximation used in DFPT: non-adiabatic effects have been discussed for the corresponding phonon dispersions [76, 77], but the consequences on electron–phonon coupling are not quantified and out of scope for the present work. The deformation potentials associated to the two valleys are of opposite sign: as the atoms are displaced periodically in space and time according to the A1 (or LA) phonon patterns, the two types of valleys go up and down in energy, in an out-of-phase fashion. At fixed Fermi level, this implies that the charge density difference associated to each valley is also out-of-phase (when one valley gains electrons, the other loses them). The free-carrier response to this perturbation is proportional to the total charge difference, i.e. summed over both valleys, which implies that it vanishes as the net charge density change does. We consider the isotropic response to a phonon perturbation at momentum \(q\), with the Fermi level and temperature as parameters. The deformation potential \(\delta V\) of each valley is the bare deformation potential \(\delta V^0\) minus the potential created by the total induced density of charge \(\delta n\)

\[
\delta V_k = \delta V^0_k - \nu_c \delta n \\
\delta V_Q = \delta V^0_Q - \nu_c \delta n.
\]

The induced density of charge has three contributions, one from the free carriers in each valley, and a dielectric one: \(\delta n = \delta n_K + \delta n_Q = \chi_k^D \delta V_k + \chi_Q^D \delta V_Q + \chi_{K/Q}^D (\delta V_K + \delta V_Q).\) Here, index \(Q\) refers either to the Q valley on the electron side or to the \(\Gamma\) valley on the hole side. \(\chi_{K/Q}^D\) is the independent particle susceptibility associated to either valley, computed from the band structure as described above, but limiting the integral to states belonging to just one or the other valley. This quantity depends on doping and temperature (chosen to be room temperature here).
T Sohier

and valley profile and the effective temperatures and $Q$ of the electrons and holes, with $i$ are evaluated at each doping and valley $T$ (see SI for and $K$ = $\delta g_0$ versus doping $\delta$). For $\mathbf{q}$ is tuned such that the densities of electrons is quite sensitive to the or the $K$ calculations as detailed in the SI, and the screened potential as well.

The bare potentials are extracted from DFPT calculations, crosses are the model. Here we use a much coarser 32 $\times$ 32 electron momentum grid with Marzari–Vanderbilt smearing at 0.01 Ry (as opposed to the 120 $\times$ 120 grids with Fermi–Dirac, room-temperature smearing used for mobility calculations).

This relatively simple model explains the behavior of the DFPT EPIs very well, as shown for the coupling to the A1 mode in the K valley in figure 6 (see SI for the Q valley and the LA mode, and for more details in general). For example, in the case where only one valley is occupied, the susceptibility of the other valley is zero, and the potential of the occupied valley is screened like a standard external perturbation. When both valleys are occupied, the two contributions to the induced charge density are of opposite sign, reducing the overall induced potential and thus the screening as well.

The bare potentials are extracted from DFPT calculations as detailed in the SI, and the screened potentials $\delta V_{\text{K/Q}}$ are evaluated at each doping and valley configuration, and at each $q$ point, by solving equation (2). The EPI matrix elements of the reference calculation are then corrected as follows:

$$g_{\text{new}} = g_{\text{ref}} \times \frac{\delta V_{\text{K/Q}}}{\delta V_{\text{K/Q}}}.$$ 

Note that the LA mode also has a contribution from piezoelectric coupling, but it is relatively weak and quickly screened by the standard free-carrier screening. Thus, we neglect that contribution in doped systems. This also justifies the use of a doped calculation rather than a neutral one as a reference. Indeed, neutral systems lead to larger piezoelectric contributions to the LA mode, making them a less appropriate starting point for the screening correction scheme where the piezoelectric contributions to LA are supposed to be absent. This implies a possible overestimation of the mobility towards small doping, but ensures that the main features of the mobility as a function of doping are more accurate. All other couplings are not neglected, they are simply left as they are in the reference calculation. That is, we assume them to be doping and valley profile independent.

3.2. Kerr

A finite Kerr rotation angle in semiconducting TMDs implies non-equilibrium occupation of different reciprocal space valleys. This arises from the fact that, while the orbital and pseudospin magnetic moment are responsible for the magnetization, they change sign between valleys (as do the spins). It is indeed this change in sign that is responsible for TMDs being able to absorb light with opposite circular polarization in the K$^+$ and K$^-$ valleys.

The first step is the preparation of excited configurations of electrons and holes, designed to reproduce the quasi-equilibrium states achieved once both have scattered within the “spin allowed” valley where they are created, but before they have had time to travel outside to opposite spin valleys (several ps), or to recombine (10’s of ps to ns). This is achieved by promoting electrons to the conduction bands by selecting a value for the shift in the system’s chemical potential $\mu_i$ and the effective temperatures $T_i$ of the electrons and holes, with $i$ = e, h. Then, assuming that the two systems are at thermal equilibrium, their temperatures are set equal $T_e = T_h$. Energy levels are then populated according to Fermi distributions, which yield the densities of excited carriers.

$\mu_h$ is tuned such that the densities of electrons and holes match (otherwise the system is no longer neutral). Once both densities are equal, the populations of electrons and holes in the complement $K^+(K^-)$ and $Q^+(Q^-)$ are set to zero, to ensure that only the main valleys are populated with excited carriers.

Finally two excited state configurations were created for each ($\mu_e, T_e; \mu_h, T_h$) quartet, as shown in figure 7, with excited electrons and holes populating either the K$^+$ and Q$^+$ or the K$^-$ and Q$^-$ valleys shown in figure 1. The configurations are then used to calculate the correction to the energy levels induced by the presence of excited carriers. We then evaluate the Kerr amplitude using the Yambo package [78].

Figure 6. Effect of the multivalley screening on the electron–phonon coupling for the A1 phonon mode in electron-doped WS$_2$ versus doping $n$ and valley profile $\Delta K Q$ comparison of the model to DFPT. We pick K as an initial state, and a small $|q| = 0.025$ Å$^{-1}$ in the $\Gamma$–K direction. Dots are direct DFPT calculations, crosses are the model. Here we use a much coarser 32 $\times$ 32 electron momentum grid with Marzari–Vanderbilt smearing at 0.01 Ry (as opposed to the 120 $\times$ 120 grids with Fermi–Dirac, room-temperature smearing used for mobility calculations).
Figure 7. Amplitude of the Kerr rotation angle at the A exciton for WS$_2$ (top) and WSe$_2$ (bottom) from the Q$^+$ (red) and Q$^-$ (blue) configurations for $T = 40$ K, $\mu_e = 0$ eV, and $\Delta K_Q = 0$ eV. The symmetry of the signal reflects the opposite spin polarization of each valley occupation configuration. The inset triangles show the regions of the Brillouin zone where electrons are promoted to the conduction bands in either the Q$^+$ or Q$^-$ configurations. The black dashed vertical line marks the energy of the A exciton for each system.

4. Conclusion

We propose an ab initio model of electron–phonon scattering with both doping and valley profile as parameters. We exploit this model to evaluate the impact of valley profile on electronic transport and Kerr rotation signal in the semiconducting TMDs: MoS$_2$, MoSe$_2$, WS$_2$, WSe$_2$. On the transport side, our findings show that all systems behave similarly for both electron and hole doping. Namely, the doping-dependent mobility peaks around $8 \times 10^{12}$ cm$^{-2}$, and the height of the peak depends on the valley profile. The results give quantitative guidelines to optimize the mobility, and point to the possibility of determining the valley profile from doping-dependent transport measurements. Regarding the Kerr rotation amplitude, our data shows that this quantity is extremely sensitive to small changes in the valley profile, as the differences in band energies make it easier or harder to populate opposite spin populations. This suggests that Kerr amplitude measurements can be used to track the changes in valley profile of the TMD upon encapsulation, and from there infer the changes in effective thickness or strain.

Data availability statement

The data that support the findings of this study are openly available at the following URL/DOI: https://doi.org/10.24435/materialscloud:er-mz [70] on https://archive.materialscloud.org.

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