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Electronic dynamics in graphene and MoS₂ systems

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We performed wave packet dynamical calculations for graphene- and MoS₂ monolayers by a new formulation of the split-operator FFT method utilizing *ab-initio* band structure results into the kinetic energy operator. While the time dependent dynamics is available through the solution of the time dependent Schrödinger equation in wave packet dynamics, the energy dependent dynamics is calculated by the application of the time-energy Fourier trans-

form to the wave function. Time dependent probability results show an anisotropic spreading of the probability density current. The magnitude and angular dependence of the anisotropy is dependent i) on the process creating the initial wave packet (e.g. injection from an STM tip or scattering on an impurity) and ii) on the details of the band structure.

1 Introduction One of the possible material families of the post-Silicon era is the family of the two dimensional (2D) materials. Whereas graphene was the first member of this group, transition-metal dicalchogenides (TMDCs) provide a large variety of properties [1,2]. In order to analyse measurement results and to design nanoelectronic devices, it is important to precisely understand the dynamics of electrons in these materials. Wave packet dynamics (WPD) [3] is a flexible method to simulate electronic dynamics and transport phenomena at the nanoscale which is capable of calculating realistic models containing several hundred atoms already on a personal computer. Given a Hamiltonian and an initial wave function, WPD yields the time dependent wave function by the solving of the time dependent Schrödinger equation. By application of time-energy Fourier transform, the energy dependent dynamics is also available. During the past two decades [4], we have been performing WPD calculations for many sp² Carbon nanosystems. In all these calculations the physical system was modelled by some kind of $V(\vec{r})$ potential function. In the first approximation [5,6] this potential function was a simple jellium potential. This was suitable to model the geometric effects in Scanning Tunneling Microscopy (STM) imaging of carbon nanotubes (CNTs) [5,6].

STM offers the possibility to study both the atomic and electronic structure of the same nanostructure with sub-nanometer resolution. This unique advantage of the method is

also its greatest difficulty: the influence of the geometry and the electronic structure is always intimately mingled in STM images and Scanning Tunneling Spectroscopy (STS) curves. In order to include electronic structure into the WPD calculation, we began using a local atomic pseudopotential [7] modelling the π electron bands of the sp² carbon sheet. This potential has two major advantages: i) it brings the specific electronic dynamics (linear dispersion near the K points for electrons near the Fermi energy (E_F), trigonal warping for hot electrons, etc) of the π bands into the WPD calculation and ii) makes it possible to handle localized defects. We utilized this potential for many calculations, networks of CNTs [8], modelling tip induced anisotropic electron dynamics during the STM imaging of graphene [9], and scattering of electrons by grain boundaries in graphene [10,11].

Atomic pseudopotential WPD, though an effective and capable method, is limited by the availability of a suitable local atomic pseudopotential function, which is not readily available for every material systems. The Hamiltonian, however, contains both a kinetic- and a potential energy operator, $\hat{H} = \hat{K} + \hat{V}$ and modifying \hat{K} provides us an additional degree of freedom in describing electronic dynamics. In our pseudopotential Schrödinger WPD calculations the kinetic energy was quadratic in $|\vec{k}|$ and the peculiarities of the graphene band structure (linear near K point, etc) was

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introduced into the Hamiltonian by the $V(\vec{r})$ potential function. Dirac equation WPD calculations [12], however, utilize a kinetic energy linear in $|\vec{k}|$, hence these calculations correctly reproduce the small excitation energy (linear) band structure of graphene without any potential term. By addition of potential, and vector potential terms, Dirac equation WPD calculations can nicely reproduce a large variety of effects important in graphene, such as charge puddles [13] and magnetic phenomena [14].

Possibilities of exploitation of the kinetic energy operator does not end by using a quadratic or linear $|\vec{k}|$ dependence. The $E = E_n(\vec{k})$ dispersion relation contains the full electronic structure information for a given crystalline material and the dispersion relation is readily available from state-of-the-art band structure calculations for practically any material. In this paper we present a general method to include the band structure information into the WPD calculation. First we demonstrate the method for the case of a graphene sheet, modelled by the simplest tight-binding band structure, then apply the method to analyse electronic dynamics on monolayer MoS₂ utilizing state of the art *ab-initio* results.

The present calculations are aimed at illustrating the spreading of a localized WP in the context of transport. These do not intend to explore the relaxation of hot electrons prepared e.g. by optical excitations [15]. Localized WPs can be injected, for example, onto a 2D sheet by an STM tip. Zero temperature calculations exclude electron scattering by phonons. Bloch equation calculations [15,16,17], however, should be more appropriate to deal with phonons at finite temperature than time dependent Schrödinger equation.

Elastic collisions by impurities like Oxygen and other defects could be included by introducing appropriate scattering potentials in the Hamiltonian [13]. This will be done in a future step. The present paper can be considered as a preparatory stage for more realistic calculations.

The organization of the paper is as follows. Section 2 gives an outline of the WPD method and of the dispersion relations used for graphene and MoS₂. In Sec. 3 numerical results are presented for spreading of the WPs on graphene and MoS₂. Section 4 is devoted to the discussion of the results.

Hartree atomic units are used in all formulas except where explicit units are given. SI units are used, however, in all the figures and numerical data.

2 Calculation methods

2.1 The split-operator FFT method

In this method the time development of the $\psi(\vec{r}, t)$ wave function is computed from the time-dependent 3D Schrödinger equation using the split operator Fourier-transform method [18]

$$\psi(\vec{r}, t + \Delta t) = e^{-i\hat{H}\Delta t} \psi(\vec{r}, t)$$

$$e^{-i(\hat{K} + \hat{V})\Delta t} \cong e^{-i\hat{K}\Delta t/2} e^{-i\hat{V}\Delta t} e^{-i\hat{K}\Delta t/2} + O(\Delta t^3)$$

where the potential energy propagator is a simple multiplication with $\exp(-iV(\vec{r})\Delta t)$ for local potentials, and the effect of the kinetic energy propagator $\exp(-i\hat{K}/2\Delta t)$ is dealt with in k space by multiplying the momentum space wave function by $\exp(-i|\vec{k}|^2 \Delta t/4)$. We are able to obtain all measurable quantities from the $\psi(\vec{r}, t)$ time dependent wave function, such as the probability density $\rho(\vec{r}, t)$, the probability current $\vec{j}(\vec{r}, t)$, etc. By applying a t-E Fourier transform the (more conventional) $\psi(\vec{r}, E)$ wave function and energy-dependent measurables are also available. One of the advantages of the split operator method is the norm conservation of the WP, which is necessary to calculate accurate transport values during the simulation time.

The $|\vec{k}|^2$ term in the kinetic energy expression is nothing else but the free space $E = |\vec{k}|^2/2$ dispersion relation of an electron. Indeed, the split operator method exactly reproduces the free-space evolution of the electronic wave packet for the case of $V(\vec{r}) \equiv 0$ zero potential. Why not changing the dispersion relation to any $E = E_n(\vec{k})$ function, which correctly describes the electronic structure of the specific material? This can be done, indeed, and this makes it possible to go beyond the Dirac-like physics of graphene and to study such effects in WPD as trigonal warping and anisotropic spreading.

2.2 Calculation of the dispersion relations We demonstrate the method in two examples: i) tight-binding (TB) description of graphene and ii) Density Functional (DFT) treatment of Molybdenum-disulphide (MoS₂).

For our graphene calculations we used the simplest possible TB approximation [19], with its six double Dirac cones at the six K points, as seen on Fig. 1a.

For the case of monolayer MoS₂ a more sophisticated DFT calculations were performed using the Vienna ab initio simulation package (VASP) [20]. In DFT calculations the results depend on the approximation of the exchange correlation potential that describes the many-body interaction between electrons. In the present paper we used the general gradient approximation (GGA) in the scheme of PBE (Perdew-Burke-Ernzerhof) functional [21]. Previous calcu-

lations show [22,23], that this functional gives proper description of the MoS₂ including the indirect-direct band gap transition when the bulk material is thinned to a monolayer, in good agreement with experimental findings [24].

In the calculation we used projector augmented wave (PAW) pseudo-potentials [25] and the kinetic energy cut-off for the plane wave expansion was 500 eV. The Brillouin-zone was sampled using with 8×8×1 Monkhorst–Pack mesh [26]. Figure 1b-c shows the calculated dispersion relations of the valence- and conduction bands. In order to focus on basic effects of the anisotropic WP spreading we neglected spin-orbit coupling – we will switch it back in a subsequent work.

3 Results In this section we analyse the time development of the direct space probability density function $\rho(x, y; t)$. The momentum space probability density function $\rho(k_x, k_y; t)$ remains constant, equal to its initial value, $\rho(k_x, k_y; t) = \rho(k_x, k_y; t_0)$. This is because the potential is zero in this calculation, $V(\vec{r}) \equiv 0$.

All of our initial WPs studied in this paper are localized to a small spatial region in the direct space. The initial $\rho(x, y; t_0)$ direct space probability density is a simple Gaussian for all the cases, but the complex phase of the wave function is a different function of the position in the different cases (K, K', Q, Γ points), which corresponds to different initial momentum space wave functions, dictated by the analytic properties of the Fourier transform.

Figure 2 shows the time development of the $\rho(x, y; t)$ probability density of the WP on graphene, when the initial state is a Gaussian located at one of the K points, i.e. the initial momentum-space wave function is

$\psi(\vec{k}, t = 0) = N e^{-(\Delta x)^2 |\vec{k} - \vec{k}_K|^2}$, where N is a normalization constant and Δx is the direct space width of the Gaussian. The corresponding momentum space width of the Gaussian is $\Delta k = (1/2)(1/\Delta x)$. The spreading of the WP shows an anisotropic time development, it splits into three parts, each moving away from the centre, showing a three-fold symmetry. This is because of the trigonal warping effect around the K point (cf Fig. 1a).

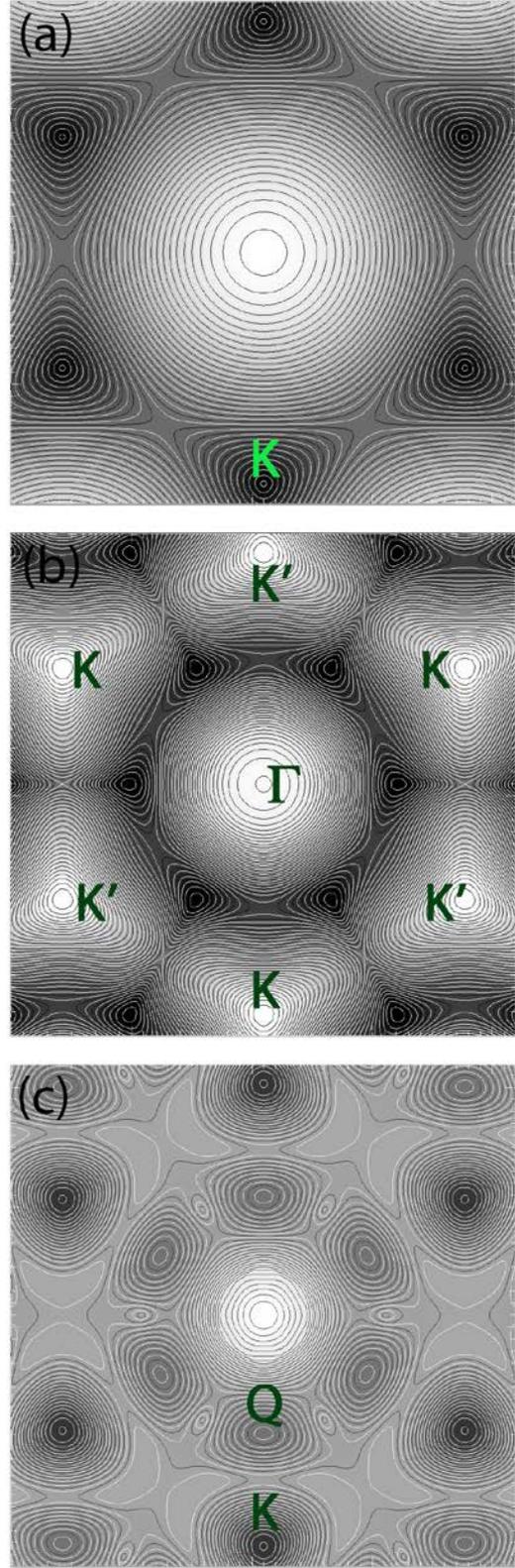


Figure 1 $E(k_x, k_y)$ dispersion relation for graphene (tight-binding model) and MoS₂ (DFT PBE calculation). (a) graphene

conduction band, $E \in [0, 9] eV$ (b) MoS₂ valence band $E \in [-1.06, -0.10] eV$, (c) MoS₂ conduction band $E \in [1.58, 2.70] eV$. Black corresponds to energy minimum and white to energy maximum of the bands. There are 80 evenly spaced isoenergy contour lines in each figure. Those points of the Brillouin zone, which were used as wave packet starting points are marked with letters. (See the text for details.)

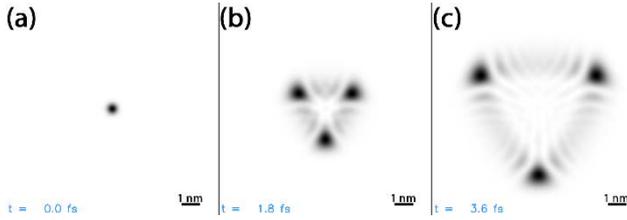


Figure 2 Time development of the direct space probability density of the wave packet on the graphene sheet. The momentum space wave function (not shown) is a Gaussian centred on the K point (marked in Fig.1a). White corresponds to zero probability and black to the maximum probability. Each snapshot is individually normalized. Size of the presentation window is 11.52 nm. Width of the initial Gaussian is $\Delta x = 0.187 nm$.

The magnitude of the anisotropy depends on the Δx parameter. A large Δx (i.e. a small Δk) corresponds to a thin WP in momentum space, which means that the majority of the WP resides in the linear dispersion range around the K point, hence the WP evolution shows only negligible anisotropy. A small Δx (i.e. a large Δk) represents, by contrast, a wide dispersion in momentum space, the majority of the WP falls outside the linear dispersion range and that yields a considerable anisotropy in the time development. Indeed, the first two terms of the Taylor series expansion of the graphene TB dispersion relation around the K point is

$$\Delta k + \Delta k^2 \frac{\pi}{2} \sin 3\varphi,$$

which shows that the larger Δk is,

the larger the three fold symmetric term becomes.

The case of the MoS₂ monolayer is more complicated. In this direct gap semiconductor there is a hole conduction at the six K points of the valence band, but the Γ point of the valence band is very close in energy to the K points. The lowest energy points of the first conduction band are also at the K points, but the Q points (halfway between Γ and K) are close in energy to the K points.

Figure 3 shows the $\rho(x, y; t)$ snapshots at $t=14.5$ fs at four characteristic initial WP positions at the MoS₂ Brillouin zone for the valence- and conduction bands. The momentum space width of the initial WP was the same for all these four calculations (but larger as the value used for graphene, cf. Fig.2). When the initial WP is centred in the momentum

space at the K point, we see trigonal warping both at the valence- and conduction bands (Figs. 3a and 3c), though the valence band case shows a higher amount of anisotropy. This can be understood by looking at the dispersion relations shown on Fig.1, where the trigonal warping is considerably higher around the K points of the valence band (Fig.1b) than at the conduction band (Fig.1c). Figure 3b shows the $t=14.5$ fs probability density snapshot when the initial WP is centred at the Γ point of the valence band. We see a slow isotropic spreading here, which can be explained by the slow and isotropic variation of the energy around the valence Γ point, cf. Fig.1b. Isoenergy contours around the Q point of the conduction band (halfway between Γ and K, cf. Fig. 1c) shows a peculiar distorted twofold symmetric pattern. This is the cause of the probability density pattern seen on Fig.3d.

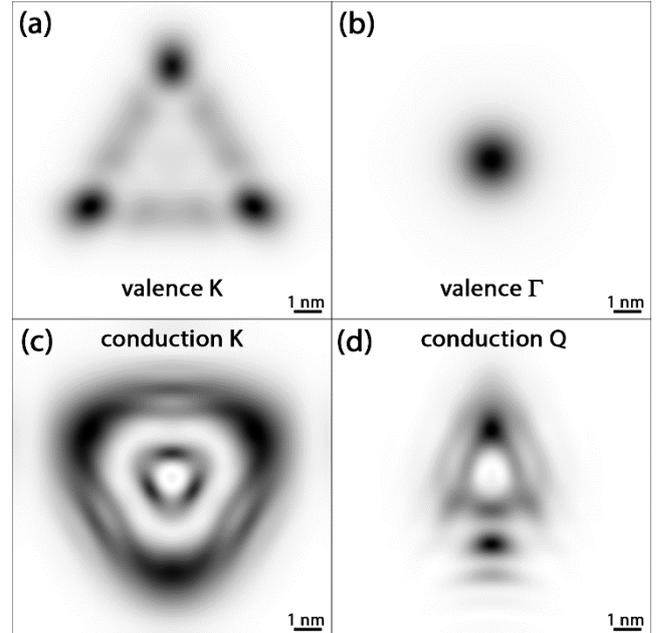
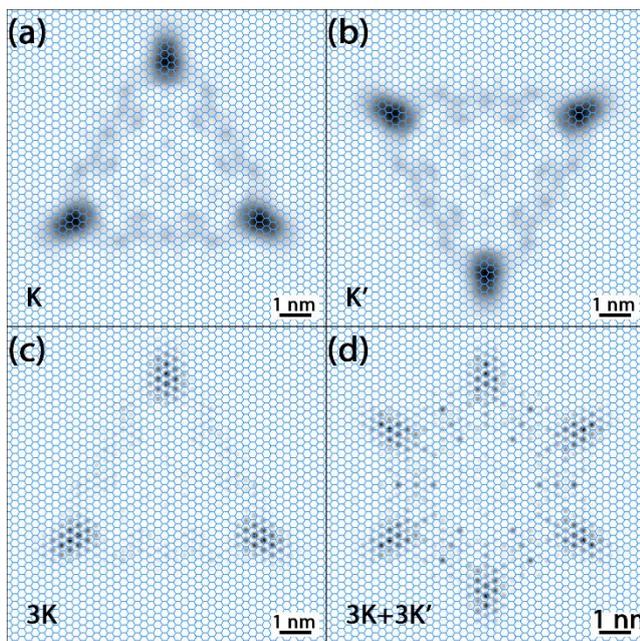


Figure 3 MoS₂ direct space probability density snapshots ($t=14.5$ fs) for different scenarios. (a) K point at the valence band (cf Fig.1b), (b) Γ point at the valence band (cf Fig.1b), (c) K point at the first conduction band (cf Fig.1c), (d) Q point at the first conduction band (cf Fig.1c). White corresponds to zero probability and black to the maximum probability. Each snapshot is individually normalized. Size of the presentation window is 11.52 nm. Width of the initial Gaussian is $\Delta x = 0.374 nm$.

Figure 4 shows $\rho(x, y; t)$, the probability density of the direct space WP for $t=14.5$ fs for different initial wave packets for the case of the valence band. When $\psi_0(\vec{k})$ is a Gaussian centred on one of the K points (Fig.4a), we see a trigonal warping effect similar to Fig.3a. This time, however, we choose a smaller direct space width for the Gaussian (the Δx parameter), which means a larger width in momentum space. This explains that the anisotropy is larger in Fig.4a

1 than in Fig.3a. When the Gaussian is centred on a K' point
 2 (Fig.4b), a similar pattern emerges, but rotated by 60°. The
 3 subsequent two images show situations, when the initial
 4 wave packet is a superposition of three Gaussians centred
 5 on the three K points (Fig.4c) and when it is a superposition
 6 of six Gaussians, centered on the three K and the three K'
 7 points (Fig.4d). The three K points time development is very
 8 similar to that obtained for one K point, but a small wave-
 9 length, atomic scale modulation is seen on the probability
 10 density – similar to the HOMO-LUMO patterns calculated
 11 by DFT [27]. This is caused by interference of the plane
 12 wave parts of the three Gaussians in direct space. The three
 13 K – three K' points case (Fig.4d) has a similar atomic
 14 modulation, but the envelope function shows a six-fold sym-
 15 metry in this case.



18 **Figure 4** Direct space probability density snapshots ($t=14.5$ fs) for
 19 different initial momentum space WP configurations in the MoS₂
 20 valence band, shown on Fig.1c. (a) Single Gaussian on a K point,
 21 (b) single Gaussian on a K' point, (c) Superposition of 3 Gaussians
 22 at the 3 K points, (d) Superposition of 6 Gaussians at the 3 K and
 23 3 K' points. The atomic lattice is shown by thin lines. White cor-
 24 responds to zero probability and black to the maximum probability.
 25 Each snapshot is individually normalized. Size of the presentation
 26 window is 10.02 nm. Width of the initial Gaussian is
 27 $\Delta x = 0.187\text{nm}$.

31 **4 Discussion** Anisotropic WP spreading is seen for all
 32 the three studied dispersion relations: the graphene conduc-
 33 tion band, MoS₂ valence- and conduction bands, but their
 34 magnitude is different. The width of the graphene conduc-
 35 tion band is nearly ten times as much as that of the MoS₂
 36 valence- and conduction bands (9 eV vs. 0.96 eV and 1.12
 37 eV), hence the same initial direct space Gaussian width Δx
 38 corresponds to a much larger energy distribution of the initial
 39 WP for the graphene than for MoS₂. Indeed, trigonal
 40 warping effects on graphene become apparent only for hot
 41 electrons having energy $E_F \pm 1.2\text{eV}$ but the energy range
 42 of the linear dispersion is only ± 0.1 eV in MoS₂. The shape
 43 of the dispersion relation around the K point is also different
 44 for the MoS₂ valence- and conduction bands [28]: the iso-
 45 energy contours are much more distorted at the valence band
 46 which results a more pronounced anisotropy of the WP
 47 spreading for the case of the valence band, which affect
 48 transport in slightly p-doped configurations.

49 The specific form of the initial wave packet in a real sys-
 50 tem depends on how this initial state was created. In order
 51 to create a localized electronic state on the otherwise perfect
 52 2D crystal lattice one needs some kind of localized pertur-
 53 bation. This localized perturbation can be, for example, an
 54 apex of an STM tip [9], or a structural defect [27]. As we
 55 showed earlier [9], the tunnelling from the STM tip to the
 56 graphene surface is a rather complex phenomenon and the
 57 details of this process determine, what will be the initial
 58 state of the further evolution of the WP on the graphene (or
 59 MoS₂) sheet. The specific initial state is determined by many
 60 factors, e.g. the position of the tip and the bias voltage.
 61 These initial states correspond to the different initial mo-
 62 mentum space wave functions analysed in this paper.

63 Indeed, a localized WP can be created by inserting elec-
 64 trons from the STM tip into a slightly p-doped MoS₂ sheet.
 65 As we have shown earlier for the case of graphene sheet [9],
 66 when the STM tip is above a center of a hexagon, the initial
 67 WP will have 6-fold symmetry, resulting a 6-fold symmetry
 68 in WP spreading (like in Fig. 4d), when it is above a carbon
 69 atom, the initial WP has 3-fold symmetry, causing a 3-fold
 70 symmetric spreading (like in Fig. 3c). If, however, the tip is
 71 placed to a point with no particular symmetry, e.g. displaced
 72 slightly from the “above the atom” position, this can lend a
 73 linear momentum to the WP specified by the direction of the
 74 above mentioned displacement. The linear momentum is
 75 represented in the direct space wave function as a plane
 76 wave component, which corresponds to a displacement of
 77 the wave function in momentum space. This way we can
 78 design “tailor made” initial WPs by carefully choosing the
 79 position of the STM tip.

80 In the case of slightly p-doped MoS₂, transport will arise
 81 from few electrons around the K and K' points of the first
 82 Brillouin zone. In the present non spin polarized calculation,
 83 K and K' are perfectly equivalent, which means we have to
 84 deal with a symmetric combination of the 6 points (Fig.4d).
 85 In the presence of spin polarization, the valence bands
 86 around K and K' points will be equally populated, but with
 87 electrons of opposite spins. For each spin, the current will
 88 spread like shown in Fig. 4c, but the total current will aver-
 89 age according to Fig. 4d.

90 Further localized perturbations may come from struc-
 91 tural defects, e.g. Sulphur vacancies, which cause mid-gap

states in MoS₂ [29]. These mid gap states have triangular and hexagonal atomic scale patterns observed recently in STM measurements [30]. Ghorbani et al analysed [27] the effect of different localized defects on the MoS₂ transport for currents in the zigzag- and armchair directions, utilizing a non equilibrium Green function DFT approximation. Their results show a considerable anisotropy (difference of the zigzag- and armchair current) for all studied localized defects.

5 Conclusions Investigating the anisotropy of the current in TMDC materials in the absence and presence of defects has a considerable importance. Our WPD calculations based on ab-initio calculated energy dispersion relations highlight an intrinsic anisotropy in the MoS₂ band structure at low energies, which might give important information for future TMDC based nanoelectronic devices.

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