



Weyl Semimetals (WSM) for Electronics Applications

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Final Report

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14. ABSTRACT Discovery of Dirac materials introduced phenomena usually regarded in the context of the high-energy physics to the everyday energy scale. The effective mass of electrons in such materials is small comparing to a typical excitation or even absent. In this case, a variety of phenomena emerges that are absent in conventional materials. Among these phenomena, the emergent conservation of helicity, the sign of the mutual orientation of the momentum of the particle and its spin, attracts a special attention. In the case of vanishing effective mass, helicity obeys a conservation law similar to the conservation law of the electric charge but independent of it. The challenge in controlling helicity is that in usual Dirac materials states with opposite helicities are difficult to distinguish. The situation drastically changed when recently materials with removed degeneracy between helicities, Weyl semimetals (WSM), were synthesized and experimentally tested. Such materials open the way to govern the density of helicity, axial charge, and its flow, axial current. The research funded by grant FA9550-16-1-0363 investigated application potential of WSM. It was shown that states with different helicities can be separated and thus the axial current can be turned into conventional electric current thus establishing axial-current conversion. Additionally, the problem of transport of Weyl fermions in structures with restricting geometry was investigated. It was found that generally in the presence of the boundary a gap in the spectrum of propagating modes opens thus making carriers massive. At the same time, this induced mass does not break the helicity conservation law. This shows that in WSM the flow of electric and axial charges can be controlled opening ways for helicity based weyltrionics.			
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Abstract:

Discovery of Dirac materials introduced phenomena usually regarded in the context of the high-energy physics to the everyday energy scale. The effective mass of electrons in such materials is small comparing to a typical excitation or even absent. In this case, a variety of phenomena emerges that are absent in conventional materials. Among these phenomena, the emergent conservation of helicity, the sign of the mutual orientation of the momentum of the particle and its spin, attracts a special attention. In the case of vanishing effective mass, helicity obeys a conservation law similar to the conservation law of the electric charge but independent of it. The challenge in controlling helicity is that in usual Dirac materials states with opposite helicities are difficult to distinguish. The situation drastically changed when recently materials with removed degeneracy between helicities, Weyl semimetals (WSM), were synthesized and experimentally tested. Such materials open the way to govern the density of helicity, axial charge, and its flow, axial current. The research funded by grant FA9550-16-1-0363 investigated application potential of WSM. It was shown that states with different helicities can be separated and thus the axial current can be turned into conventional electric current thus establishing axial-current conversion. Additionally, the problem of transport of Weyl fermions in structures with restricting geometry was investigated. It was found that generally in the presence of the boundary a gap in the spectrum of propagating modes opens thus making carriers massive. At the same time, this induced mass does not break the helicity conservation law. This shows that in WSM the flow of electric and axial charges can be controlled opening ways for helicity based weyltronics.

Subject Terms: Weyl semimetals, helicity, axial charge, axial current, beyond-CMOS, weyltronics

1. Introduction

Conventional materials

The major factor determining transport properties of solids is the number of electron states in a vicinity of Fermi level. In equilibrium, no macroscopic flow of electrons exists and, therefore, in order to create such flow, electrons must be excited over their equilibrium distribution. However, electrons with energies well below the Fermi level (comparing to the characteristic energy scale $k_B T$, where k_B is the Boltzmann constant and T is the temperature), cannot acquire small excitation energy. Indeed, in this case, they would have energy corresponding to already occupied states, which is prohibited by the Pauli principle. In turn, well above the Fermi level, where excitation of electrons is not constrained by the Pauli principle, the electron states are not populated thus making their contribution to the response negligible.

An elementary classification of materials as conductors and insulators is, therefore, based on the relation between the Fermi level and the energy bands characterizing electron states in the solid. In metals, such as copper or silver, the Fermi level is inside the band and, therefore, metals have high electric and thermal conductivities. In insulators, for instance, silicon dioxide (SiO_2) or crystal sodium chloride (NaCl), the Fermi level is inside the wide, conventionally more than 4 eV, bandgap separating valence and conduction (below and above the Fermi level, respectively) bands, for example, $\Delta \approx 8.9$ eV in SiO_2 and $\Delta \approx 8.5$ eV in NaCl .

Such picture establishing a relation between the band diagram of a solid and its transport properties is sufficient for dealing with materials with sharp conducting or insulating properties. However, it requires refinement when the band gap is not too wide (Δ is smaller than 4 eV). Materials with $0 < \Delta < 4$ eV are semiconductors, for example, silicon (Si , $\Delta \approx 1.1$ eV) and gallium arsenide (GaAs , $\Delta \approx 1.5$ eV). Since the Fermi level is essentially the electrochemical potential for electrons, its position on the band diagram noticeably depends on doping (concentration of donor or acceptor impurities) and the external electric potential. These are core properties laying in the ground of semiconductor electronics.

Further decreasing of the gap width results in overlap of the valence and conduction bands. Such materials are called semimetals. Usually, for instance in bismuth (Bi) and graphite (an allotrope of carbon, C), this occurs when the extremal points of the bands are located at points with different momenta. In this case, the direct gap, the separation between points in conduction and valence bands with the same momentum, preserves. As a result, the electron density of states at the energy range corresponding to overlapping bands is small and the materials demonstrate properties characteristic for both semiconductors and metals.

New generation of materials: Dirac and Weyl semimetals

Recently, a series of new materials enriching the canonical understanding of solids started to attract significant attention. Among them, a special place is taken by semimetals with the extremal points of the conduction and valence bands residing at the same momentum and separated by a small or even absent

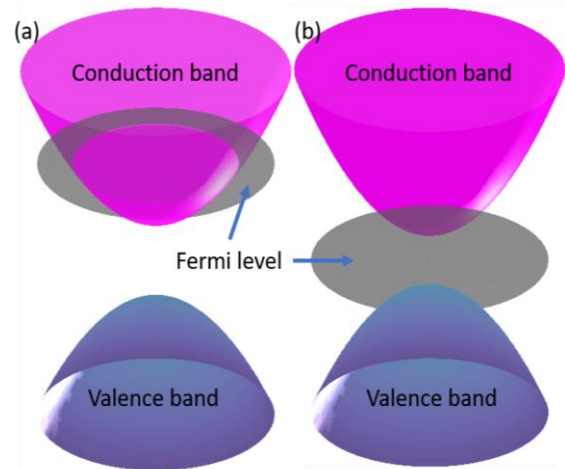


Fig. 1. The band diagrams of (a) conductor and (b) semiconductor (or dielectric) in a vicinity of the extremal points of the valence and conduction bands.

gap. The important feature of such materials is that near the extremal points of the valence and conduction bands, the electron states with a good accuracy are described by a Dirac equation generalized to account for a possible lack of rotational symmetry. As a result, the dynamics of low-energy excitations is similar to ultra-relativistic quantum particles. This brings concepts that previously were thought of only in the context of very high energies into the “everyday” energy range.

The most famous and well-studied example of such materials is graphene, a one-atom thick carbon layer. Due to its lattice structure, the band diagram of graphene has distinctive Dirac cones touching each other at the K -points of the Brillouin zone (see Fig. 2). Due to the linear dispersion law near these points, electrons behave like massless fermions. Such particles are called Weyl fermions after the physicist who first considered the massless limit of the Dirac equation. Respectively, the touching point of the conduction and valence bands is called the Weyl point.

The lattice symmetry makes some of the K points physically indistinguishable leaving in graphene only two distinct Dirac cones. By analogy with the description of electron states in semiconductors, the electron states corresponding to different K points are referred to as corresponding to different valleys. Within each valley, the electron is described by a two-component wave-function, which satisfies a 2D massless Dirac equation. Traditionally components of such wave-functions are interpreted as the amplitudes of the spin to be up and down in a chosen basis. In graphene, however, these components do not correspond to an actual spin but rather emerge from the amplitudes for the electron to be found near the two atoms in the elementary cell of the graphene. Therefore, in order to distinguish from the true spin of the electron, the emergent spin is called pseudo-spin.

The fact that in graphene low-energy excitations behave like Weyl fermions leads to plethora peculiar properties of graphene. Two such properties, which are tightly related with the main subject of the reported research, should be especially emphasized. First, this is the phenomenon of Klein tunneling: the ability of the electron to propagate through a potential barrier of arbitrary height and width without any reflection. It’s worth noting that graphene provided the way for the first experimental demonstration of Klein tunneling. While its theory is dated by early days of development of the quantum theory, an experimental confirmation had to be delayed by almost a century. In order to compensate the gap due to the free electron mass $\Delta_e = 2m_e c^2$, a potential of a great strength unavailable in controllable experiment is required. For example, the Coulomb interaction between two elementary charges reaches Δ_e at the distance $\sim 10^{-15}$ m, which is of the order of the proton size. At the same time, in graphene, the electron effective mass is zero, which makes the Klein tunneling relevant for arbitrary height of the barrier and makes it available for a direct experimental observation.

Second, the electron pseudo-spin and its momentum can only be (in the absence of external fields) either parallel or anti-parallel, corresponding to states with positive and negative helicity, respectively. Both these phenomena are directly related to zero effective mass of the electron in graphene.

It is important to emphasize, therefore, that the zero-mass property is not stable in 2D systems and can be broken by an external potential or by structural modifications. This circumstance drew a

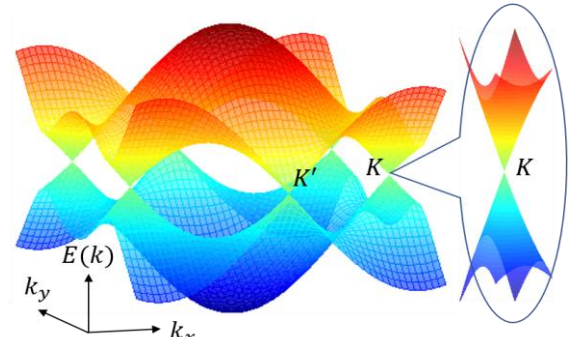


Fig. 2. The band diagram of graphene in the tight-binding approximation demonstrating the emergence of the Dirac points. The inset shows a vicinity of one of the points, where the energy spectrum has the form of Dirac cones.

significant attention to the problem of finding 3D analogs of graphene, or, more precisely, 3D solid state realizations of Dirac materials with zero mass. The raised dimensionality leads to fundamental differences between properties of the electron states in a 3D Dirac material and graphene: in 3D materials, the Dirac cones are not repelled by moderate perturbations but are simply shifted.

In addition to stabilizing the zero-mass property, increasing dimensionality leads to emergence of a new conservation law. Weyl fermions not only can be characterized by a definite helicity, but the spatial distribution of helicity satisfies a conservation law similar to that of the electric charge. Therefore, the helicity and the helicity current are often called the axial charge and the axial current, respectively.

In the limit of zero mass, the Dirac equation decouples into the pair of Weyl equations corresponding to particles with different helicities. This implies the Dirac points emerging, for instance, in graphene, in fact, unite two Weyl points. As will be shown below, when these points coincide, it is difficult to distinguish Weyl fermions with different helicities. Therefore, a significant attention was paid to finding materials where the Weyl points are not degenerate (see Fig. 3). Conventionally, the materials with separated Weyl points are called Weyl semimetals (WSM).

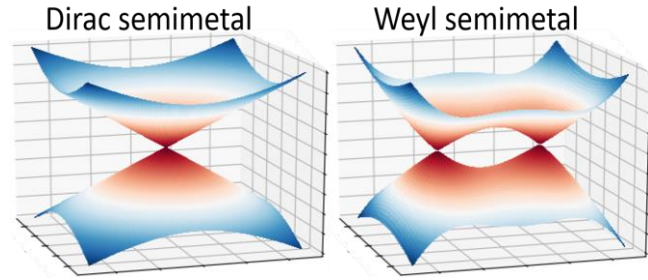


Fig. 3. Band diagrams of a Dirac and Weyl semimetals near the pair of the Weyl points. In Dirac semimetals, the Weyl points coincide, while in WSM the Weyl points are separated.

The general properties, which WSM should satisfy (broken inversion or time reversion symmetries, and substantial spin-orbit coupling) were recognized relatively soon. Thus, the search went along two strategical directions: 1) breaking the time reversion symmetry by means of macroscopic magnetic field and 2) breaking the inversion symmetry in specially constructed materials. Among studies following the first path should be mentioned $\text{Y}_2\text{Ir}_2\text{O}_7$ [1], HgCr_2Se_4 , where the ground state was expected to be ferromagnetic [2], $\text{Bi}_{1-x}\text{Sb}_x$ with applied magnetic field, where transport measurements showed strong indication of the material being a WSM [3], and heterostructures made of interlaced layers of magnetically doped topological insulator and regular insulators [4]. Breaking of the inversion symmetry was explored in materials with careful chemical or structural composition: $\text{TlBi}(\text{S}_{1-x}\text{Q}_x)_2$ with $\text{Q} = \text{Se}$ or Te , where the inversion symmetry is broken by the growth technique [5], $\text{QBi}_{1-x}\text{Sb}_x\text{Te}_3$ with $\text{Q} = \text{La}$ or Lu , where the WSM phase was expected for $0.39 < x < 0.42$ and $0.41 < x < 0.46$, respectively [6], and multilayer HgTe/CdTe heterostructures with applied strain, where the phase depends on the relation between the strain and the layers thickness [7]. The characteristic feature of these materials is that they either rely on macroscopic magnetic ordering or require careful compositional or structural tuning. Both these circumstances greatly diminish the practicality of these materials in mass applications.

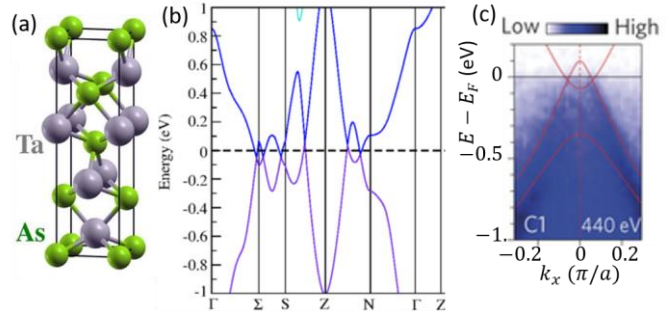


Fig. 4. (a) The structure of TaAs consists of four layers without the inversion symmetry. (b) The band diagram of TaAs demonstrating split Weyl points near the Fermi level (dashed line). (c) The photoemission spectrum of TaAs showing split Weyl points. Courtesy of [12] and [13].

The situation, changed drastically after discovery TaAs (see Fig. 4) and NbAs with the inversion symmetry broken in stoichiometric, single-crystal material [8-18]. These materials are free from complications mentioned above, which endows them with a promising application potential.

2. Research performed under exploratory grant

Before discovery of solid state realizations of WSM, 3D Weyl fermions with non-degenerate helicities were purely theoretical objects attracting attention mostly within the context of high-energy physics. This left the problem of potential applications of WSM completely out of the scope of researchers. But even after discovery that TaAs, TaP, NbAs, and NbP are WSM, the main attention of researchers remains concentrated on fundamental aspects of dynamics of Weyl fermions. As a result, theoretical foundations of applications of WSM are virtually inexistent and yet to be laid out. In the performed research, the investigation was directed toward outlining general properties of transport of Weyl fermions in WSM from the perspective of controlling the flow of electric charge and helicity with two guiding questions:

1. What is needed in order to distinguish electrons with different helicities?

M. Eremenchouk and P. Mazumder, “Helicity-dependent scattering in layered Weyl semimetals,” *Physics Letters A*, vol. 381, pp. 2866–2871, 2017.

2. What are specific features of signal propagation in WSM structures?

M. A. Khan, M. Eremenchouk, J. Hendrickson, and M. N. Leuenberger, “Electronic and optical properties of vacancy defects in single-layer transition metal dichalcogenides,” *Physical Review B*, vol. 95, p. 245435/1-12, 2017.

M. Eremenchouk and P. Mazumder, “Weyl fermions in cylindrical wires,” *Physical Review B*, vol. 97, p. 035429/1-7, 2018.

Separating states with different helicities [19]

[M. Eremenchouk and P. Mazumder, “Helicity-dependent scattering in layered Weyl semimetals,” *Physics Letters A*, vol. 381, pp. 2866–2871, 2017]

Assuming implemented utilizing helicity for transmitting information, how this information stored in helicity can be read? Helicity conserves only in special media and outside of such media any information recorded in helicity will be lost. In order to read helicity encoded information, it must be transformed into a charge-based encoding, which can be perceived by conventional devices or by a human. What are the principal requirements for such axial-electric conversion?

A general direction, along which an answer to such question can be found, is suggested by the form of the equation of motion governing Weyl fermions near a pair of Weyl points in a WSM

$$\left[\frac{\partial}{\partial_0} + i e V(\mathbf{r}) + i \gamma^5 q_0(\mathbf{r}) \right] \Psi(\mathbf{r}) = -v \boldsymbol{\alpha} \cdot [\nabla + i e \mathbf{A}(\mathbf{r}) + i \gamma^5 \mathbf{q}(\mathbf{r})] \Psi(\mathbf{r}),$$

where $\Psi(\mathbf{r})$ is the four-component spinor describing the electron, e is the charge of the electron, $V(\mathbf{r})$ and $\mathbf{A}(\mathbf{r})$ are scalar and vector potentials of the electromagnetic field, and $q_0(\mathbf{r})$ and $\mathbf{q}(\mathbf{r})$ are separations between the Weyl points in energy and momentum space, respectively. Here, we have introduced the Dirac matrices in the chiral representation

$$\gamma^5 = \begin{pmatrix} -\hat{1} & 0 \\ 0 & \hat{1} \end{pmatrix}, \quad \boldsymbol{\alpha} = \begin{pmatrix} -\boldsymbol{\sigma} & 0 \\ 0 & \boldsymbol{\sigma} \end{pmatrix},$$

where $\hat{1}$ is a 2×2 unit matrix, and $\boldsymbol{\alpha} = \alpha_x \mathbf{e}_x + \alpha_y \mathbf{e}_y + \alpha_z \mathbf{e}_z$ with $\alpha_{x,y,z}$ defined in terms of the Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Choosing the chiral representation for the Dirac matrices allows us to represent

$$\Psi(\mathbf{r}) = \begin{pmatrix} \psi_-(\mathbf{r}) \\ \psi_+(\mathbf{r}) \end{pmatrix},$$

where $\psi_{\pm}(\mathbf{r})$ are two-component spinors corresponding to Weyl fermions with respective helicities.

The important feature of the equations of motion is that they show that the separation between the Weyl points enters in the same manner as the electromagnetic field but, instead of the electric charge, the energy depends on helicity of the particle. Due to the presence of γ^5 , the sign of the potential induced by the separation between the Weyl points depends on the helicity of the particle. In other words, the separation between the Weyl points creates a helicity dependent scalar (given by the energy difference between the points) or vector (the separation in the momentum space) potential, or, shortly, an axial potential.

This suggests that in specially constructed structures an axial force can be emulated, which will spatially separate particles with opposite helicities. Since the flux of the particles with fixed helicity is just a conventional electric current, such separation will create separated electric currents, which can be detected using conventional devices.

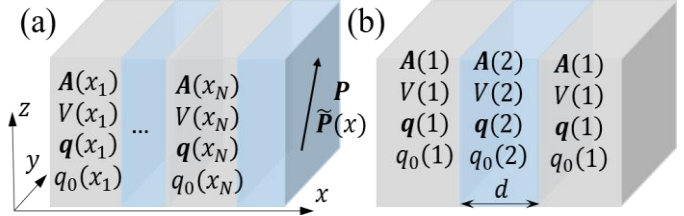


Fig. 5. (a) Geometry of a WSM layered system. (b) A three-layer system: a layer of width d is sandwiched between semi-infinite layers.

To investigate this mechanism, we considered in [19] propagation of Weyl fermions in a multilayer 3D Weyl structure (see Fig. 5), where different layers are characterized in general by different scalar and vector potentials and separations between the Weyl points. In order to tackle the problem of propagating Weyl fermion in such structures, we have developed a formalism of spinor transfer matrices. The specific feature of this formalism is that it represents the spinor wave function in terms of spin states defined by the potential inside each layer instead of, say, representing them in some chosen basis. While unconventional, this formalism provided means for developing a compact description of propagation of Weyl fermions in multilayered structures. Applying this formalism to a three-layer system (Fig. 5(a)), we have shown that scattering on the middle layer is described by transmission and reflection coefficients of surprisingly simple Lorentz-like form

$$|t_{\xi}(\mathbf{P})|^2 = \frac{1}{1 + f_{\xi}^2(\mathbf{P})}, \quad |r_{\xi}(\mathbf{P})|^2 = \frac{f_{\xi}^2(\mathbf{P})}{1 + f_{\xi}^2(\mathbf{P})},$$

where $\xi = 1$ and $\xi = -1$ correspond to positive and negative helicities respectively, $\mathbf{P}$ is the momentum of the electron in the plane of the layers and

$$f_{\xi}^2(\mathbf{P}) = (\mathbf{P} - \mathbf{P}_{\xi}^{(K)}) \cdot \hat{X}_{\xi}^2 \cdot (\mathbf{P} - \mathbf{P}_{\xi}^{(K)})$$

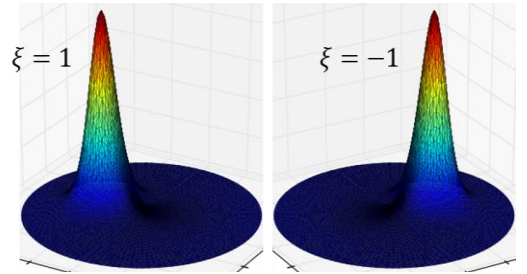


Fig. 6. Transmission through a WSM layer vs in-plane momentum for different incoming helicities: (a) positive and (b) negative.

with some tensor $\hat{X}_\xi^2$, which rather smoothly changes with the in-plane momentum and is explicitly provided in [19]. These expressions show that the dependence of scattering on the in-plane momentum is determined by the helicity dependent “Klein momentum”,

$$\mathbf{P}_\xi^{(K)} = \bar{\mathbf{P}}^{(K)} + \xi \Delta \mathbf{P}^{(K)}.$$

When the in-plane momentum coincides with the Klein momentum, the electrons pass through the layer without any scattering for arbitrary width of the barrier (it appears only inside tensor $\hat{X}_\xi^2$) and the form of the scattering coefficients shows that the transmission coefficient should have a form of a resonance localized near the Klein momentum. Thus, if $\Delta \mathbf{P}^{(K)} \neq 0$, resonant transmission of particles with opposite helicities occurs at different in-plane momenta (see Fig. 6) and the outgoing particles become directionally separated between rays with particles of definite helicity (see Fig. 7). Since, as has been discussed above, such rays correspond to conventional charge flow, they can be detected by conventional devices, which constitutes a foundation for axial-electric conversion. For example, with the help of the external electromagnetic field, the scattering layer can be made fully transparent for particles with one helicity and virtually opaque for particles with another.

An important conclusion following from this consideration is that in order to perform axial-electric conversion, it is necessary to have $\Delta \mathbf{P}^{(K)} \neq 0$. We have shown in the paper that this can be achieved only in the presence of the axial potential. In other words, we have shown that WSM are indispensable for implementing axial-electric conversion and their availability opens ways for using helicity for representing and transmitting information.

Boundary conditions for Dirac electrons [20]

[M. A. Khan, M. Erementchouk, J. Hendrickson, and M. N. Leuenberger, “Electronic and optical properties of vacancy defects in single-layer transition metal dichalcogenides,” *Physical Review B*, vol. 95, p. 245435/1-12, 2017]

In possible applications utilizing specific features of Weyl fermions, the massless electron states will be implemented in structures with restricting geometry. Moreover, in the same way as in conventional CMOS technologies, the target scale of devices will be in the nanometer range. In systems

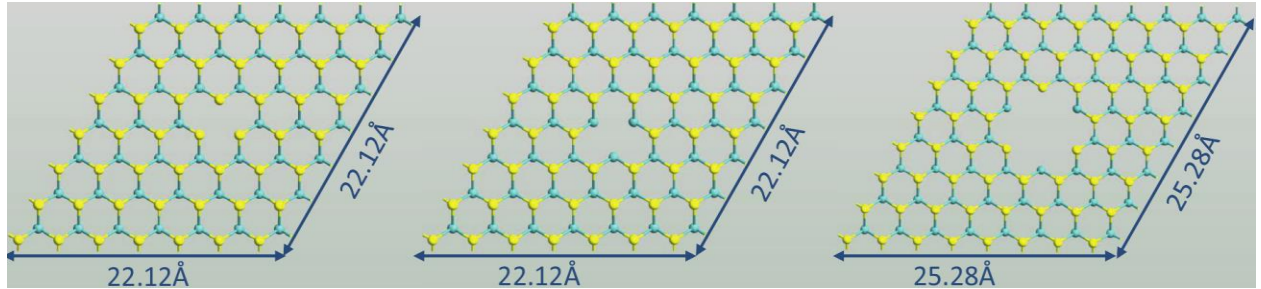


Fig. 8. Anti-dots of different structure in a single sheet MoS₂. From left to right: Mo vacancy in a 7 × 7 supercell, S₂ vacancy consisting of a pair of S atoms, hexagonal 3 × 3 MoS₂ anti-dot in an 8 × 8 supercell

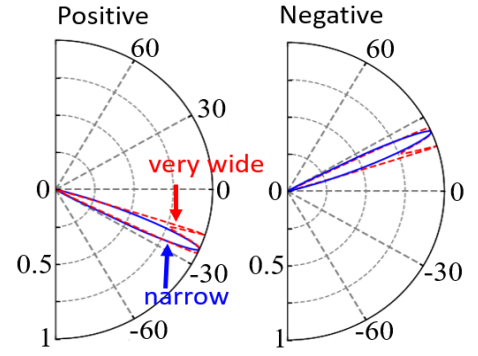


Fig. 7. Angular dependence of the transmission coefficient for electrons with different helicities. In wide structures, additional resonances corresponding to Fabry-Perot resonances become apparent.

of such geometry, the problem of the effect of the boundary conditions on the states of Weyl fermions is of great importance. One aspect of this problem was considered as a part of an investigation involving teams from several universities.

One of the problems directly related to the effect of a surface of a finite size structure is the problem of electron states in Dirac materials with anti-dots, which depending on the dimensionality of the material have the form of cavities (3D materials) or holes (2D materials). This problem attracted a lot of attention in the context of engineering localized states in Dirac materials. In [20], Dr. Erementchouk's contribution was the development of a model explaining the formation of defect states bound to anti-dots in a single sheet of a transition metal dichalcogenide (see Fig. 8). Numerical simulations utilizing density functional theory (DFT) revealed the presence of defect levels emerging inside the gap in the band structure of pristine MoS₂ (see Fig. 9) and other materials of the form MX_2 , where M is a transition metal such as molybdenum and tungsten and $X = S, Se, Te$ (sulfur, selenium, and tellurium).

With the help of this model, it was found that the levels appearing inside the bandgap do not exhaust all defect states. A more thorough description, accounting that the single sheet of MoS₂ has the form of three monoatomic layers, showed that one has to distinguish states with different parities with respect to the middle layer formed by the Mo atoms. The band diagrams for different parities do not coincide and, in fact, the gap in the

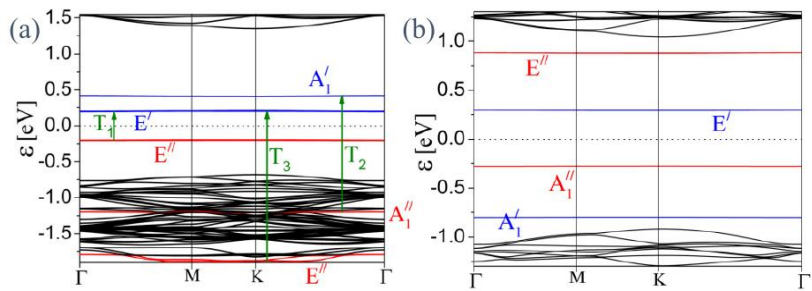


Fig. 9. Band structure in the presence of different kinds of anti-dots. The energy is counted from the Fermi level. (a) Mo vacancy. (b) S₂ vacancy. Red (blue) lines show odd (even) states. Arrows indicate transitions corresponding to resonances in the out-of-plane component of the optical susceptibility.

spectrum of even states (with the width $\Delta = 1.9$ eV) is completely contained inside the gap for odd states (with the width $\Delta = 3.2$ eV). Since removing individual atoms does not break the symmetry with respect to the middle layer, the defect states can be classified according to their parity as well. As a result, the defect states should be regarded together with the band diagrams with matching parity and may appear hidden in the case of overlapping bands and gaps.

In order to demonstrate physical consequences of existence of parity preserving defect states, the optical selection rules governing transitions between various defect states were found and the optical response was evaluated using first principle simulations. The transitions between states with different parity determine the out-of-plane component of the optical susceptibility and, therefore, it was not surprising that this component is the most affected by the emergent defect states. The numerical simulations shown in Fig. 10(b) confirmed the predictions of the analytical models.

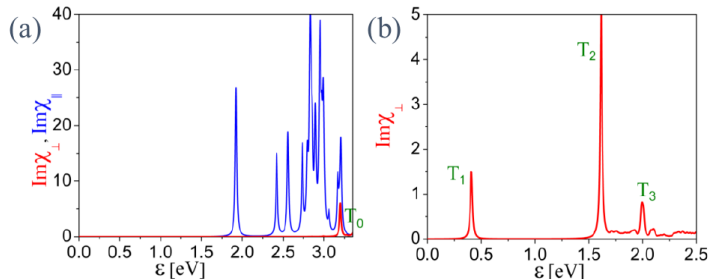


Fig. 10. (a) Resonances of in-plane (blue line) and out-of-plane (red line) components of the optical susceptibility in pristine MoS₂. (b) The out-of-plane component of the optical susceptibility when a Mo vacancy is present: the resonances are caused by transitions from the valence band to the defect states.

From the perspective of investigation of potential applications of WSM, this work revealed qualitative differences between Dirac and conventional materials, where particles are governed by the Schrodinger equation. The sole fact of emergence of defect states bound to anti-dots is highly non-trivial from the "canonical" point of view. Indeed, anti-dots, or impenetrable boundaries in general, in conventional materials can be represented by an infinitely strong repulsive potential. It is well-known, however, that bound states cannot appear in a repulsive potential and, thus, in conventional materials anti-dots cannot directly support bound states. In [20], the problem was approached from the perspective of an infinite-mass model suggested originally for studying neutrino billiards. This was sufficient for the objectives of this research, where it was used for demonstration of emergence of defect states in a 2D Dirac material with anti-dots of arbitrarily small radius.

Emergence of mass in thin WSM wires [21]

[M. Erementchouk and P. Mazumder, "Weyl fermions in cylindrical wires," *Physical Review B*, vol. 97, p. 035429/1-7, 2018]

The investigation in the previous paper showed that the problem of boundary conditions in WSM structures with restricting geometry is far from being self-evident. Therefore, a more systematic study of the finite-size effect specifically from the perspective of propagation of Weyl fermions was in order.

At the formal level, the difference between conventional and Dirac materials becomes apparent when the conditions imposed at the boundary of the anti-dot are considered. At the impenetrable boundary, as well as at the surface of an infinite repulsive potential, a solution of the Schrodinger equation must vanish as this is required by the continuity of the wave function, which must satisfy a second order differential equation. The Dirac equation, however, is of the first order with respect to the spinor wave function and, if the space outside of the anti-dot is a free space, spinor vanishing at a boundary must vanish everywhere. Thus, boundary conditions governing solutions of the Dirac equation cannot be inferred from the Schrodinger equation.

The physical origin of such discrepancy is the Klein tunneling. An attempt to represent a void by a scalar potential barrier would simply raise the level of the Dirac sea inside the void. As a result, instead of blocking propagation into the prohibited region, such barrier would create new propagating channels. Therefore, a scalar potential cannot represent a void and a more general class of matrix potentials must be considered.

The main physical requirement imposed on the spinor wave function in the presence of a hard boundary is the absence of currents into and out of the prohibited region. Such requirement is sufficient for formulating the correct form of the boundary condition for the Schrodinger equation, since, due to the continuity of a scalar wave function, it can be reduced to the requirement of vanishing wave function at the boundary. In the case of the Dirac equation, however, enforcing zero current does not constitute a valid boundary condition since current is not linear in wave functions. Because of this, a superposition of two solutions satisfying the zero-current condition may not satisfy this condition. Indeed, for a Dirac particle the direction of current is determined by the direction of its spin. As a result, any state with the spin at the

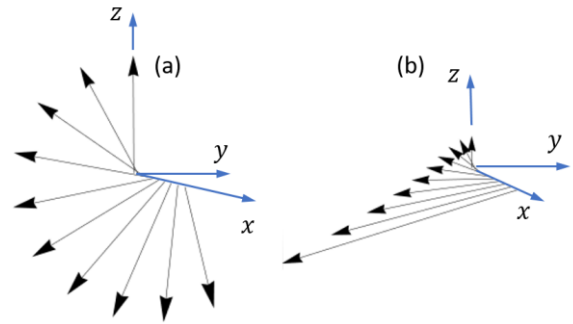


Fig. 11. The variation of the spin in a state propagating in a WSM wire with the axis parallel to the z -axis along the radius (the x -axis) in (a) extended and (b) surface modes.

boundary of the prohibited region oriented in the plane tangent to the boundary yields no current into or out of the prohibited region. On the other hand, by superimposing states with non-coinciding spins, a state with arbitrary orientation of the spin can be obtained. Thus, superpositions of states with zero current across the boundary may produce states with an arbitrary oriented current. This argument is of particular importance for Weyl fermions in WSM wires. In [21], it was shown that propagating modes of Weyl fermions in cylindrical wires have a characteristic spin structure shown in Fig. 11. At the axis of the wire, the spin is oriented along the axis and, with moving away from the center, the spin revolves around the radius of the wire. Thus, each propagating state in a cylindrical wire with necessity has the electron spin tangent to the surface. As shown above, however, this does not mean that they represent admissible states.

More detailed analysis of hard boundary conditions revealed that there is a manifold of boundary conditions that may govern solutions of the Dirac equation at the surface of an impenetrable region. In [21], it was shown that at each point of the WSM surface the spinor must be an eigenvector of a 4×4 Hermitian matrix

$$\hat{M}(\mathbf{v}_+, \mathbf{v}_-, \Lambda, \chi) = \cos(\Lambda) \begin{pmatrix} \mathbf{v}_+ \cdot \boldsymbol{\sigma} & 0 \\ 0 & \mathbf{v}_- \cdot \boldsymbol{\sigma} \end{pmatrix} + \sin(\Lambda) \begin{pmatrix} 0 & e^{i\chi} R_n(\theta) \\ e^{-i\chi} R_n^{-1}(\theta) & 0 \end{pmatrix},$$

where $\mathbf{v}_\pm$ are unit vectors lying in the plane tangent to the surface at the chosen point, $R_n(\theta)$ is the rotation operator around the outward normal to the surface, θ is the angle between $\mathbf{v}_+$ and $-\mathbf{v}_-$ (so that the rotation by θ makes $\mathbf{v}_-$ anti-parallel to $\mathbf{v}_+$), and χ is a phase. The obtained parametrization of the boundary conditions and the derived general dispersion equation relating the energy of the Weyl fermion and its momentum along the wire were applied for investigation of features of the propagating modes that hold for all boundary conditions.

It was found that despite the restricted motion in the transverse direction, the spectrum of Weyl fermions remains gapless when helicities are decoupled or, equivalently, when each helicity is characterized by a definite pinned spin state at the surface.

The situation changes drastically, however, when the boundary conditions include coupling between helicities. In this case, it was found [21] that a gap opens in the fermion spectrum with the width

$$\Delta(\Lambda) = \frac{\hbar v_F}{r_B} \cdot \frac{\sin(\Lambda)}{\cos(\Lambda) \cos(\beta) + \cos(\delta)},$$

where $\hbar$ is the Planck constant, v_F is the Fermi velocity, r_B is the radius of the wire, δ is the angle between $\mathbf{v}_+$ and $\mathbf{v}_-$ (so that $\delta = \theta - \pi$), and β is the angle between $\mathbf{v}_+ + \mathbf{v}_-$ and the axis of the wire. The dependence of the width of the gap on the matching angle θ for the case of strong coupling, $\Lambda = \pi/2$, is shown in Fig. 12.

Moreover, excitations at the bottom of the upper branch and the top of the lower branch have the form of massive excitations with the mass equal to the width of the opened gap. It must be noted in this regard, that while the width of the gap and the

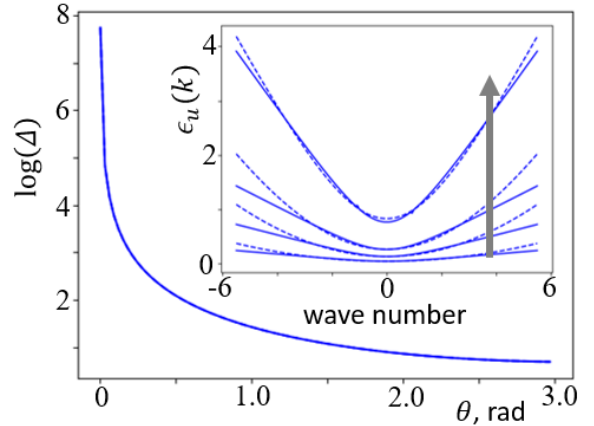


Fig. 12. The boundary induced mass as a function of the matching angle θ . The inset shows the upper branch of the massive excitations, found numerically (solid lines) and analytically (dashed lines) for different values of the matching angle (the arrow shows the variation of the branch with increasing θ).

acquired effective mass vanish in the limit of a bulk structure with a flat surface, this does not imply that the acquired mass is small unless the wire is extremely thin. The value of the induced mass depends on detailed characteristics of the boundary conditions and may even diverge (the separated branches become flat), when a special condition is met.

The developed picture of the Weyl fermion propagating states in cylindrical wires was used in [21] for establishing the character of the low-energy excitations as a phase diagram on the plane of parameters defining the separation between the Weyl points (see Fig. 13). It shows that, depending on the separation, the upper and the lower branches formed by the boundary induced gap can be occupied by states of different shape. For example, when the Weyl points are well separated in the momentum space (the upper region in Fig. 13(a) or the lower region in Fig. 13(b)), both branches are occupied by the edge modes, which are localized near the surface of the wire. The exact form of the boundary conditions determines the boundaries (the oblique straight lines in Fig. 13) between different “phases” of the low-energy states. Fig. 13 shows that virtually regardless of the precise form of the boundary conditions, for moderate separations between the Weyl points, the low-energy states are bulk modes extending over the whole cross-section of the wire. As will be discussed below, this has important implications for current carried by WSM wires.

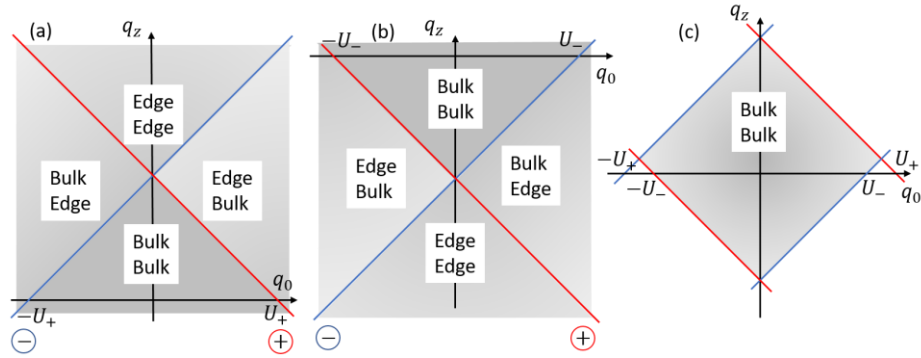


Fig. 13. The dependence of the structure of states occupying the (a) upper and (b) the lower (b) branches of the excitations gapped due to the boundary induced coupling on the separation between the Weyl points and on the boundary conditions. Panel (c) shows diagrams for different branches superimposed to indicate the region where all states have the same structure.

This analysis has shown that while the Weyl points in 3D WSM are stable with respect to moderate perturbations, the restricting geometry may constitute a strong perturbation that breaks down the massless character of the propagating modes. An important circumstance, however, must be emphasized. Despite the boundary induced coupling between helicities and an opened gap in the spectrum, this does not break the helicity conservation law *inside* the wire. This suggests that WSM structures with restricted geometry may present a unique combination where the gap in the spectrum coexists with conserving helicity.

3. Conclusion. Benefits of WSM for information processing

Three-dimensional materials with zero effective mass of electrons introduce ultra-relativistic quantum theory into the context of information processing. One of the unique feature of these materials is the emergence of a new class of charge, helicity, independent from the electric charge. The separation between the Weyl points in WSM leads to significant consequences. From the dynamical point of view, the separation manifests itself as a helicity dependent external field, often called an axial field. This leads to dynamical distinguishability of Weyl fermions with different helicities and establishes a full analogy between the helicity and the electric charge. From the perspective of potential applications, WSM are

shown in the performed research to present a missing link connecting conventional, non-relativistic world with ultra-relativistic electrons in materials with massless electrons.

One of the findings of the performed research is especially worth to emphasize. In materials with massless electrons, the problem of controlling the flow of electrons is non-trivial and challenging. Due to the phenomenon of Klein tunneling, creating a potential barrier is not sufficient to stop electrons. In 2D materials, this difficulty can be resolved by inducing the gap (and, hence, mass) by an external field. Such approach in 3D materials, however, can barely be undertaken. First, the property of zero-mass is more resilient in 3D materials with respect to perturbations. Second, the sole introduction of mass defeats the effectively ultra-relativistic behavior of carriers. For example, it would break conservation of helicity, disturb spin locking and so on. It was shown in the performed research, however, that a gap in the spectrum can be induced through the finite-size effect, which preserves ultra-relativistic features. This suggests that there are additional mechanisms of controlling the flow of Weyl fermions in 3D materials besides those explored in the context of 2D materials. A complete exploration of such mechanisms from the perspective of weyltronics is one of the objectives of future work.

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Helicity-dependent scattering in layered Weyl semimetals



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ABSTRACT

Weyl fermions are characterized by definite helicity, a relation between orientation of the spin and momentum. We investigate controlling helicity utilizing helicity-dependent dynamics due to separation between the Weyl points. We study transport properties of a multilayer structure formed by piece-wise constant scalar and vector potentials and separations between the Weyl points. We show that the transmission spectrum is determined by a relation between the electron momentum and momenta corresponding to Klein tunneling, when the barrier is fully transparent regardless of its width. The helicity dependence of the “Klein momenta” is shown to yield a helicity filtering effect.

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1. Introduction

Experimental finding of non-stoichiometric crystals demonstrating properties of Weyl semimetals (WSM) [1–6] sparked a significant interest in possible weyltronics applications, a special kind of devices employing specific features of electron excitations in WSM. Low-energy electron states in WSM behave as Weyl fermions, massless Dirac electrons, which is one of the main points of interest for novel applications [7,8]. Due to their massless character, Weyl fermions can be characterized by definite helicity, a tight relation between orientation of the electron spin and its momentum. An important property, which sets WSM apart from other Dirac materials is that the points of zero energy for particles with definite helicity, commonly known as Weyl points, are non-coinciding in WSM. This property together with topological protection of Weyl points makes helicity in WSM a promising candidate for carrying information in digital processing applications [9,10]. At the same time, such applications require flexible control over helicity, which is a non-trivial task because in the “classical” limit there is no field directly coupled to helicity. This raises a general question about controllability of helicity in WSM.

From this perspective, a special attention is drawn to axial anomaly [11–16], a phenomenon of breaking chiral symmetry of a quantized Dirac field in parallel external electric and magnetic fields. As a result of this anomaly, there is a flux of particles be-

tween Weyl points with opposite chiralities [17,18]. In the present paper, we explore an alternative approach based on the fact that separation of Weyl points in WSM induces different dynamics of states with different helicities thus making them distinguishable at the single-particle level. In order to reveal this effect, we study transport properties of WSM multilayer structures from the perspective of helicity dependent scattering. Similar systems have been studied previously [19,20] in the context of multilayer structures formed by modulated scalar potential with the main attention paid to mismatching boundaries between propagating and tunneling regimes of states with different helicities. In the present paper, we consider a general situation with piece-wise constant spatial distributions of scalar and vector potentials and separations between the Weyl points and show that the phenomenon of Klein tunneling leads to more distinguished manifestation of the helicity-dependent dynamics.

The paper is organized as follows. In Section 2, we adopt the equation of motion governing propagation of electron in WSM multilayer structures for application of the spinor transfer matrix approach and obtain the transfer matrix through a layer. In Section 3, we apply this result for deriving transmission and reflection coefficients of a three-layer structures. We show that as functions of the in-plane momentum they can be presented in a characteristic Lorentzian form with helicity dependent parameters. When penetration through the barrier is due to tunneling, the resonant in-plane momentum is complex and cannot be reached, so that the variation of scattering coefficients with the momentum is rather gradual. In the opposite case, the resonant momentum is real and when it is reached the barrier becomes transparent independently of its width. This Klein tunneling occurs at, generally

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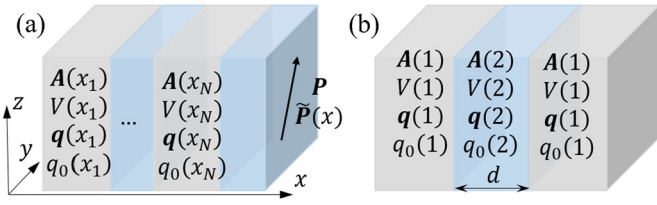


Fig. 1. (a) Geometry of a WSM layered system. (b) A three-layer system: a layer of width d sandwiched between semi-infinite layers.

speaking, oblique and helicity dependent directions. In Section 4, we show that this effect may lead to strong helicity filtering property. The main contribution of the paper is to establish a relation between prominent features in transmission spectra of WSM multilayers and the mutual arrangement of the Weyl points and to show that the helicity of electrons propagating through the structure can be controlled by external scalar and vector potentials.

2. Weyl fermions in layered structures

A layered WSM structure, schematically shown in Fig. 1, is characterized by piece-wise constant parameters varying along one dimension while being constant along other two. Because of this, the in-plane components of the momentum constitute good quantum numbers, thereby effectively reducing the problem to one-dimensional. In turn, the spatial variation of the spinor wave function across the layers is conveniently described by spinor transfer matrices. This approach was presented for a 2D Dirac equation in [21] and here we only outline its extension for treating Weyl fermions.

A general equation describing Dirac electron in a layered medium is

$$i\gamma^0 \left[\partial_0 + ieV(x) + i\gamma^5 q_0(x) \right] \psi = -i\gamma \cdot \left[\nabla + ie\mathbf{A}(x) + i\gamma^5 \mathbf{q}(x) \right] \psi, \quad (1)$$

with the piece-wise constant vector, $\mathbf{A}(x)$, and scalar, $V(x)$, potentials, and the separation between the Weyl points: $q_0(x)$ is the energy separation and $\mathbf{q}(x)$ is the separation in the momentum space. In order to emphasize the helicity property, we take the Dirac matrices γ in the chiral representation

$$\gamma^0 = \begin{pmatrix} 0 & \hat{1} \\ \hat{1} & 0 \end{pmatrix}, \quad \gamma \equiv \gamma^i \mathbf{e}_i = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ -\boldsymbol{\sigma} & 0 \end{pmatrix}. \quad (2)$$

Within this representation, Eq. (1) splits into two uncoupled equations describing states spanned by $|L\rangle = (\chi_+, 0, 0)^T$ and $|R\rangle = (0, 0, \chi_-)^T$, where $\chi_{\pm}$ are 2-spinors. These are eigenspaces corresponding to eigenvalues $\xi = +1$ and -1 , respectively, of the helicity projection operators $P_{L,R} = \frac{1}{2}(1 \pm \gamma^5)$, where $\gamma^5 = -i\gamma^0\gamma^1\gamma^2\gamma^3$ and in the chiral representation

$$\gamma^5 = \begin{pmatrix} \hat{1} & 0 \\ 0 & -\hat{1} \end{pmatrix}. \quad (3)$$

Thus, $|L\rangle$ and $|R\rangle$ span particles with left and right helicities, respectively.

Eigenstates of Eq. (1) are characterized by definite values of energy and the in-plane component of momentum, $\mathbf{P} = P_y \mathbf{e}_y + P_z \mathbf{e}_z$, so that

$$\psi(x, y, z) = \psi(x) \exp(-i\epsilon t + i\mathbf{P} \cdot \mathbf{r}). \quad (4)$$

Moreover, the projections of $\mathbf{A}$ and $\mathbf{q}$ on the x -axis can be excluded by the gauge transformation

$$\psi(x) = \exp \left\{ -i \int_{x_0}^x dx' \left[eA_x(x') + \gamma^5 q_x(x') \right] \right\} \tilde{\psi}(x). \quad (5)$$

Thus, without losing generality we can assume that vectors $\mathbf{A}$ and $\mathbf{q}$ are oriented in the (y, z) -plane. This leads us to

$$\tilde{\epsilon}(x)\psi = -i\alpha^1 \partial_x \psi + \boldsymbol{\alpha} \cdot \tilde{\mathbf{P}}(x)\psi, \quad (6)$$

where $\boldsymbol{\alpha} = \gamma^0 \gamma$, $\tilde{\epsilon}(x) = \epsilon - eV(x) - \gamma^5 q_0(x)$, $\tilde{\mathbf{P}}(x) = \mathbf{P} + e\mathbf{A}(x) + \gamma^5 \mathbf{q}(x)$, and we have rescaled the energy and the scalar potential, so that, $v = 1$.

The spinor transfer matrix approach is based on representing solutions of Eq. (6) as superpositions of propagating spinor states. It should be emphasized that the spinor transfer matrix deals with spinors rather than amplitudes of the spinor wave function. This establishes a direct relation with the states relevant for incoming and outgoing channels and thus significantly simplifies description of transport properties.

For $\psi = \begin{pmatrix} \chi_+ \\ \chi_- \end{pmatrix}$, we obtain

$$\tilde{\epsilon}_\xi(x)\chi_\xi = i\xi \sigma_x \partial_x \chi_\xi + \xi \boldsymbol{\sigma} \cdot \tilde{\mathbf{P}}_\xi \chi_\xi, \quad (7)$$

where $\xi = \pm 1$ enumerates helicities, $\tilde{\epsilon}_\xi(x) = \epsilon - U_\xi(x)$ with $U_\xi(x) = eV + \xi q_0(x)$ and $\tilde{\mathbf{P}}_\xi(x) = \mathbf{P} + \mathbf{Q}_\xi(x)$ with $\mathbf{Q}_\xi(x) = e\mathbf{A}(x) + \xi \mathbf{q}(x)$. Within a layer, spinors corresponding to the states propagating along and against the x -axis, $\chi_\xi = e^{\pm i k_\xi x} \begin{pmatrix} \tilde{\chi}_\xi^{(\pm)} \\ \tilde{\chi}_\xi^{(\pm)} \end{pmatrix}$, satisfy equations similar to the equation for a spin 1/2 particle in a magnetic field, $\tilde{\epsilon}_\xi \begin{pmatrix} \tilde{\chi}_\xi^{(\pm)} \\ \tilde{\chi}_\xi^{(\pm)} \end{pmatrix} = \boldsymbol{\sigma} \cdot \mathbf{h}_\xi^{(\pm)} \begin{pmatrix} \tilde{\chi}_\xi^{(\pm)} \\ \tilde{\chi}_\xi^{(\pm)} \end{pmatrix}$, where the effective field is defined as

$$\mathbf{h}_\xi^{(\pm)}(k_\xi) = -\xi (\pm k_\xi \mathbf{e}_x + \tilde{\mathbf{P}}_\xi). \quad (8)$$

Thus, the dispersion equation relating the local momentum k_ξ and the energy of the Weyl fermion is

$$\tilde{\epsilon}_\xi = \pm h_\xi^{(\pm)}(k_\xi), \quad (9)$$

with $h_\xi^{(\pm)} \equiv \sqrt{\mathbf{h}_\xi^{(\pm)} \cdot \mathbf{h}_\xi^{(\pm)}}$. It should be reminded that due to gauge transformation (5), vector $\tilde{\mathbf{P}}_\xi$ lies in the (y, z) -plane and, therefore, $h_\xi^{(+)} = h_\xi^{(-)} = h_\xi$.

Solutions corresponding to different branches in Eq. (9) are conveniently presented in terms of spin coherent states $|\pm \mathbf{h}_\xi^{(\pm)}\rangle$. Usually, they are defined for vectors with real components by rotating the quantization axis to align it along the defining vector [22,23]. For the system under consideration, however, it is convenient to represent the spinors with the help of dilation operators [21], emphasizing the symmetry of states $|\mathbf{h}_\xi^{(\pm)}\rangle$ and accounting for the case of imaginary h_x , which takes place when $k^2 < 0$. For $k_\xi^2 > 0$, we have

$$|\mathbf{h}_\xi^{(\pm)}\rangle = K_\xi \exp(\beta \tilde{\mathbf{P}}_\xi \cdot \boldsymbol{\sigma} / 2) |\pm \mathbf{e}_x\rangle, \quad (10)$$

where $K_\xi = \sqrt{k_\xi / |\tilde{\epsilon}_\xi|}$, $k_\xi \cosh(\beta \tilde{P}_\xi) = |\tilde{\epsilon}_\xi|$, $k_\xi \sinh(\beta \tilde{P}_\xi) = \text{sign}(\tilde{\epsilon}_\xi) \tilde{P}_\xi$.

For the tunneling regime, when $k_\xi = i\kappa_\xi$ with $\kappa_\xi > 0$, we can write

$$|\mathbf{h}_\xi^{(\pm)}\rangle = C_\xi \exp(\beta' \tilde{\mathbf{P}}_\xi \cdot \boldsymbol{\sigma} / 2) |\pm \mathbf{I}_\xi\rangle, \quad (11)$$

where $\mathbf{I}_\xi = \tilde{\mathbf{P}}_\xi \times \mathbf{e}_x / \tilde{P}_\xi$, $C_\xi = \sqrt{\kappa_\xi / \tilde{P}_\xi}$, $\kappa_\xi \cosh(\beta' \tilde{P}_\xi) = \tilde{P}_\xi$, and $\kappa_\xi \sinh(\beta' \tilde{P}_\xi) = \tilde{\epsilon}_\xi$.

The spectral point of special importance, separating tunneling and propagating regimes, is $|\tilde{\epsilon}_\xi| = \tilde{P}_\xi$. At this point, $k_\xi = -k_\xi = 0$ and, therefore, states characterized by a definite momentum do not

exhaust all solutions of Eq. (7), so that one needs to take into account the secular solution, which results in an algebraic decay of the transmission coefficient [21]. Since this takes place only at isolated spectral points, we will assume that $|\tilde{\epsilon}_\xi| \neq \tilde{P}_\xi$.

For a three-layer structure with a layer of finite width d sandwiched between semi-infinite layers (see Fig. 1(b)), following the formalism developed in [21], the transfer matrix through the middle layer is found to be

$$\hat{T}_\xi = \exp(i\tilde{\epsilon}_\xi d - \tilde{P}_\xi \mathbf{I}_\xi \cdot \boldsymbol{\sigma} d), \quad (12)$$

regardless of the regime of propagation inside the layer. The same approach can be used for a multilayer structure yielding $\hat{T}_\xi = \prod_n \hat{T}_\xi(n)$, where $\hat{T}_\xi(n)$ is given by Eq. (12) with $\tilde{\epsilon}_\xi$, d , $\tilde{P}_\xi$, and $\mathbf{I}_\xi$ taken for the n -th layer.

3. Helicity-dependent scattering

One manifestation of helicity-dependent dynamics follows straightforwardly from Eq. (9) resolved with respect to the x -component of the momentum,

$$k_\xi = \pm \sqrt{\tilde{\epsilon}_\xi^2 - \tilde{P}_\xi^2}. \quad (13)$$

For $F(\epsilon, \mathbf{P}) = (\epsilon - eV)q_0 + (\mathbf{P} + e\mathbf{A}) \cdot \mathbf{q} \neq 0$, the spectral point separating propagating and tunneling regimes depends on helicity. As a result, at given ϵ and $\mathbf{P}$, one may have $k_+^2 k_-^2 < 0$, that is only particles with one helicity may propagate [19,20]. The boundary between the regions of the phase space where only one helicity is attenuated is a plane $F(\epsilon, \mathbf{P}) = 0$. This suggests the way to maximize the effect of separating helicities based on non-overlapping bands. Let, for instance, $q_0 = 0$, then choosing the scalar potential such that $\tilde{\epsilon} \approx 0$ makes states with $\xi = 1$ propagating through the layer only when $\mathbf{P}$ is in a narrow vicinity of $-\mathbf{q} - \mathbf{A}$, while $\xi = -1$ states propagate when $\mathbf{P} \approx \mathbf{q} - \mathbf{A}$. The characteristic feature of discriminated helicities due to mismatched bands is the separation between momenta corresponding to propagating modes with different helicities proportional to the separation between the Weyl points in the momentum space.

A phenomenon of a different origin is “Klein filtering”, which is due to the tight relation between the spin of the electron and direction of its propagation and thus is inherently connected to helicity. From the transport point of view, this phenomenon is due to strong variation of transmission near the direction corresponding to Klein tunneling [24–27]. As we show below, separation of helicities in this case occurs regardless of mutual band arrangement.

For a three layer system, the scattering problem is naturally set in terms of the states introduced above. For a chosen helicity ξ , the transmission and reflection coefficients are found from

$$\hat{T}_\xi \left(\left| \mathbf{h}_\xi^{(+)}(1) \right\rangle + r_\xi \left| \mathbf{h}_\xi^{(-)}(1) \right\rangle \right) = t_\xi \left| \mathbf{h}_\xi^{(+)}(2) \right\rangle. \quad (14)$$

Here and below, 1 and 2 in the parentheses denote the semi-infinite and middle layers, respectively, described by the sets of parameters $q_0(1, 2)$, $\mathbf{q}(1, 2)$, $\mathbf{A}(1, 2)$ and $V(1, 2)$. Using Eq. (10), we obtain

$$t_\xi^{-1} = \langle -\mathbf{e}_x | e^{-\beta \tilde{\mathbf{P}}_\xi \cdot \boldsymbol{\sigma} / 2} \hat{T}_\xi e^{\beta \tilde{\mathbf{P}}_\xi \cdot \boldsymbol{\sigma} / 2} | -\mathbf{e}_x \rangle \\ = \cos(k_\xi(2)d) - i \sin(k_\xi(2)d) D_\xi, \quad (15)$$

where

$$D_\xi = \frac{1}{k_\xi(2)k_\xi(1)} [\tilde{\epsilon}_\xi(1)\tilde{\epsilon}_\xi(2) - \tilde{\mathbf{P}}_\xi(1) \cdot \tilde{\mathbf{P}}_\xi(2)]. \quad (16)$$

From $|t_\xi|^2 + |r_\xi|^2 = 1$, it follows that

$$|r_\xi|^2 \propto |D_\xi|^2 - \text{sign}(k_\xi^2(2)). \quad (17)$$

Using this expression, it can be shown that when $k_\xi^2(2) > 0$, reflection vanishes if $\tilde{\epsilon}_\xi(1)\tilde{\mathbf{P}}_\xi(2) - \tilde{\epsilon}_\xi(2)\tilde{\mathbf{P}}_\xi(1) = 0$. For helicity ξ this condition is fulfilled when $\mathbf{P} = \mathbf{P}_\xi^{(K)}$ with

$$\mathbf{P}_\xi^{(K)} = \frac{1}{\Delta U_\xi} [\tilde{\epsilon}_\xi(2)\mathbf{Q}_\xi(1) - \tilde{\epsilon}_\xi(1)\mathbf{Q}_\xi(2)], \quad (18)$$

where $\Delta U_\xi = U_\xi(2) - U_\xi(1)$.

Using the expression for $\mathbf{P}_\xi^{(K)}$, the scattering coefficients can be presented in a compact form

$$|t_\xi|^2 = \frac{1}{1 + f_\xi^2(\mathbf{P})}, \quad |r_\xi|^2 = \frac{f_\xi^2(\mathbf{P})}{1 + f_\xi^2(\mathbf{P})}, \quad (19)$$

where for $k_\xi^2(2) > 0$ we have

$$f_\xi^2(\mathbf{P}) = (\mathbf{P} - \mathbf{P}_\xi^{(K)}) \cdot \hat{X}_\xi^2 \cdot (\mathbf{P} - \mathbf{P}_\xi^{(K)}) \quad (20)$$

with tensor

$$\hat{X}_\xi^2 = \frac{\sin^2(k_\xi(2)d)}{k_\xi^2(1)k_\xi^2(2)} [\Delta U_\xi^2 + \Delta \mathbf{Q}_\xi^2 - \Delta \mathbf{Q}_\xi \otimes \Delta \mathbf{Q}_\xi], \quad (21)$$

where $\Delta \mathbf{Q}_\xi = \mathbf{Q}_\xi(2) - \mathbf{Q}_\xi(1)$.

These equations reveal the phenomenon of Klein tunneling, vanishing reflectivity for arbitrary d , when the momentum of incoming electron satisfies $\mathbf{P} = \mathbf{P}_\xi^{(K)}$. It should be emphasized that this phenomenon is different from the full transmission at “magic angles” [27]. In terms of expressions written above, the magic angles correspond to vanishing $\hat{X}_\xi^2$, which occurs when $k_\xi(2)d = \pi n$ with integer n . Thus, the magic angles are essentially Fabry–Perot resonances, while the Klein tunneling is due to matching of the spin states inside and outside of the barrier and corresponds to non-reflecting interfaces.

In order to find the condition for appearing the Klein tunneling in the transmission spectrum, one needs to take into account that $\mathbf{P}$ is constrained by the requirement that outside of the middle layer we have propagating modes. This leads to

$$\Delta \mathbf{Q}_\xi < |\Delta U_\xi|. \quad (22)$$

The obtained expressions show that, generally speaking, the in-plane momentum corresponding to Klein tunneling depend on helicities of the electron. In order to explicate this dependence, we rewrite Eq. (18) as

$$\mathbf{P}_\xi^{(K)} = \bar{\mathbf{P}}^{(K)} + \xi \Delta \mathbf{P}^{(K)}, \quad (23)$$

where

$$\bar{\mathbf{P}}^{(K)} = -\bar{\mathbf{A}} - \frac{1}{\Delta \epsilon^2 - \Delta q_0^2} (g \Delta \mathbf{A} - h \Delta \mathbf{q}), \\ \Delta \mathbf{P}^{(K)} = -\bar{\mathbf{q}} + \frac{1}{\Delta \epsilon^2 - \Delta q_0^2} (h \Delta \mathbf{A} - g \Delta \mathbf{q}), \quad (24)$$

where $g = \bar{\epsilon} \Delta \epsilon + \bar{q}_0 \Delta q_0$ and $h = \bar{\epsilon} \Delta q_0 + \bar{q}_0 \Delta \epsilon$ with the bar denoting the mean value of the respective parameters across terminating and middle layers and Δ denoting the difference between them: $\bar{\mathbf{A}} = [\mathbf{A}(2) + \mathbf{A}(1)]/2$, $\Delta \mathbf{A} = \mathbf{A}(2) - \mathbf{A}(1)$, $\bar{\mathbf{q}} = [\mathbf{q}(2) + \mathbf{q}(1)]/2$, $\Delta \mathbf{q} = \mathbf{q}(2) - \mathbf{q}(1)$, $\bar{q}_0 = [q_0(2) + q_0(1)]/2$, $\Delta q_0 = q_0(2) - q_0(1)$, $\bar{\epsilon} = \epsilon - e[V(2) + V(1)]/2$, $\Delta \epsilon = e[V(2) - V(1)]$.

Equations (23) and (24) are one of the main results of the paper. They show that propagation through the barrier is a result of an effective coupling between the helicity state of the Weyl fermion and external fields despite the absence of the direct coupling in the Hamiltonian. The origin of such coupling is the sole nature of helicity as a tight relation between momentum of the

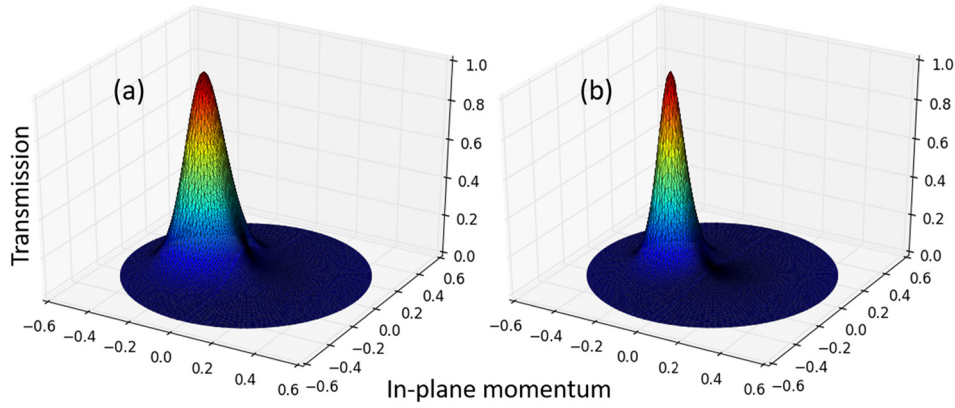


Fig. 2. The dependence of transmission through a narrow (a) and wider (b) WSM layer with $\tilde{\mathbf{P}}^{(K)} = 0$ on the in-plane component of momentum for an electron with positive helicity and fixed energy $\epsilon \gtrsim V(2)$.

particle and its spin. The Klein tunneling is a phenomenon especially suited for revealing such coupling. The Klein tunneling occurs when the spinor eigenstates are homogeneous across the structure, while the orientation of the spinors depends on local values of both external fields and separations between the Weyl points.

As follows from Eqs. (23) and (24), helicity-dependent Klein tunneling can be achieved in a variety of systems and can be controlled by parameters characterizing the barrier. For example, if the Weyl points are only separated in the momentum space with $\mathbf{q}(x) \equiv \mathbf{q}$, a potential barrier satisfying Eq. (22) yields Klein tunneling for different helicities occurring at in-plane momenta separated by $\mathbf{P}_-^{(K)} - \mathbf{P}_+^{(K)} = 2\mathbf{q}$, similar to what we have seen in the case of mismatching propagation and tunneling regimes. At the same time, it must be noted that separation between the Weyl points in the momentum space is not a necessary condition for distinct Klein tunneling directions. Indeed, if the Weyl points have different energies but correspond to the same momentum, so that $\mathbf{q}(x) \equiv 0$ and $q_0(x) \equiv q_0$, one has $\mathbf{P}_-^{(K)} - \mathbf{P}_+^{(K)} = 2\Delta\mathbf{A}q_0/\Delta\epsilon$, so that a matrix potential created by both, scalar and vector, potentials may induce helicity dependent Klein tunneling. Finally, in WSM with Weyl points separated both in energy and momentum, by varying the scalar component of the matrix potential, one can either enhance the separation between $\mathbf{P}_\pm^{(K)}$ or reduce it.

We complete the consideration of transmission properties, by a brief discussion of the case, when the electron tunnels through the middle layer, $k_\xi(2) = i\kappa_\xi$. In this case, as follows from Eq. (17), the reflection coefficient is always positive and the Klein tunneling does not take place. Equation (19) can be shown to remain valid with substituted $f_\xi^2 \rightarrow f_\xi^2 + 2\sinh^2(\kappa_\xi d)$, so that the transmission coefficient demonstrates asymptotic monotonous exponential decay with d . The discrimination between helicities, in this case, is mostly due to their non-coinciding propagating and tunneling bands as discussed above. In this case, we can represent

$$f_\xi^2(\mathbf{P}) = (\mathbf{P} - \mathbf{S}_\xi^*) \cdot \hat{\mathbf{X}}_\xi^2 \cdot (\mathbf{P} - \mathbf{S}_\xi), \quad (25)$$

where $\mathbf{S} = \mathbf{P}_\xi^{(K)} + i\Delta\mathbf{S}_\xi$ with vector $\Delta\mathbf{S}_\xi$ perpendicular to $\Delta\mathbf{Q}_\xi$ and magnitude

$$\Delta S_\xi^2 = \frac{2\kappa_\xi^2(2)k_\xi^2(1)}{\Delta U_\xi^2 + \Delta Q_\xi^2}. \quad (26)$$

Since the resonant vector $\mathbf{S}_\xi$ is complex, it is never reached and, for a generic d , transmission is determined by the tails of the Lorentz distribution.

4. Helicity filtering

Helicity-dependent directions of Klein tunneling leads to the effect of helicity filtering even when energies correspond to propagating modes of both helicities ($k_\xi^2(x) > 0$). We illustrate this effect by considering an ensemble of incoming states characterized by the same energy ϵ . The in-plane momentum, $\mathbf{P}$, is limited by the propagation condition $|\mathbf{P} + \mathbf{Q}_\xi(1)| < |\tilde{\epsilon}_\xi(1)|$, which defines a circle in the $\mathbf{P}$ -plane, centered at $-\mathbf{Q}_\xi(1)$ and with the radius $\sqrt{\tilde{\epsilon}_\xi^2(1) + Q_\xi^2(1)}$. Applying Eq. (19), we can see that the Klein tunneling manifests as a resonance in the transmission spectrum, as is illustrated in Fig. 2 for the particular case, when in the terminating layers the Weyl points are not separated, $\mathbf{q}_1 = 0$.

As follows from Eqs. (20) and (21), the resonance has approximately an elliptical shape in the $\mathbf{P}$ -plane with the major axis oriented perpendicularly to $\Delta\mathbf{Q}_\xi$. We consider the case, when the potential inside the middle layer is chosen such that $k_\xi(1)$ is small. Disregarding the non-circular shape of the resonance, we approximate

$$|t_\xi|^2 \sim \frac{\Delta P_c^2}{\Delta P_c^2 + \Delta P^2}, \quad (27)$$

with $\Delta P_c^2 \approx \frac{k_\xi^2(1)}{d^2} \left[e^2 \Delta V^2 + \Delta Q_\xi^2 \right]^{-1}$, where $k_\xi^2(1)$ is evaluated at $\mathbf{P}^{(K)}$. Thus, the width of the resonance linearly decreases with d and $|\Delta V|$ (cf. Fig. 2(a) and 2(b)) and for sufficiently narrow resonances the transmission may demonstrate significant reduction away from the resonant point. It should be noted, however, that with increasing $V(2)$ the approximation of small $k_\xi(2)$ breaks down and resonances may demonstrate complex structure due to Fabry–Perot resonances (Fig. 3(b, c)).

As a result, the flux of transmitted electrons demonstrates strong helicity imbalance, $(|t_+|^2 - |t_-|^2)/(|t_+|^2 + |t_-|^2)$, as illustrated by Fig. 3(a). It shows that the space of accessible momenta in the (y, z) -plane is separated into two regions with well-defined dominant helicity of the outgoing particles. Since for a fixed energy the in-plane momentum unambiguously determines the direction of propagation, Fig. 3(a) shows that effectively helicities of the outgoing particles are determined by their direction of propagation. The transition region between the subspaces with imbalanced helicities depends on the width of the barrier and is situated near the line $(\mathbf{P} + e\mathbf{A}) \cdot \mathbf{q} = 0$, along which there is a symmetry between different helicities. In order to show the effect of helicity discrimination in more details, we consider the case when $\mathbf{q}(1) = 0$, $V(1) = 0$ and $\mathbf{A}(x) \equiv 0$, when $\mathbf{P}_\xi^{(K)} = -\xi\epsilon\mathbf{q}(2)/V(2)$. Thus, if $P_\xi^{(K)} > \Delta P_c$, with $\Delta P_c = k(1)k(2) \left[\sin(k(2)d)\sqrt{V^2(2) + q^2(2)} \right]^{-1}$, the transmis-

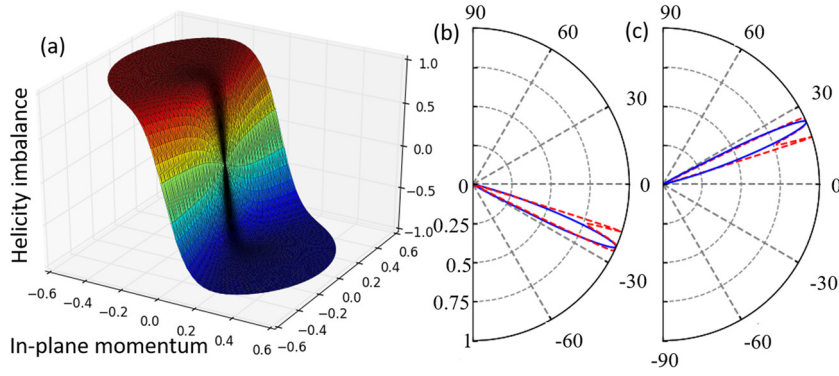


Fig. 3. (a) Helicity imbalance, $(|t_+|^2 - |t_-|^2)/(|t_+|^2 + |t_-|^2)$, as a function of the in-plane momentum. (b, c) The angular dependence of transmission of electrons with (a) $\xi = 1$ and (b) $\xi = -1$ through narrow (solid line) and wide (dashed line) barriers demonstrating complete transmission due to Klein tunneling and a Fabry–Perot resonance, respectively.

sion resonances for different helicities are well separated and the middle layer can be regarded as transmitting states of definite helicities. This is illustrated by Fig. 3(b, c), where the transmission is shown, for the case $\bar{\mathbf{P}}^{(K)} = 0$, as a function of the angle of incidence in the plane spanned by $\mathbf{e}_x$ and $\Delta\mathbf{P}^{(K)}$, that is when the in-plane momentum varies along the line $\mathbf{P}(\lambda) = \mathbf{P}_+^{(K)} + \lambda\Delta\mathbf{P}^{(K)}$. It is seen that the angular spectrum demonstrates well-defined directionality when the variation of $k_\xi(2)d$ as a function of $\mathbf{P}$ is significant on the scale determined by the eigenvalues of $\hat{X}_\xi^{-1}(\mathbf{P} = \mathbf{P}_\xi^{(K)})$. With increasing $V(2)$ or d , additional directional resonances, corresponding to the “magic angles”, appear along directions where $k_\xi(2)d = \pi n$ with integer n .

The helicity filtering effect impacts the current plowing through the barrier. The probability current carried by state ψ is $\mathbf{j}(\psi) = \psi^\dagger \boldsymbol{\alpha} \psi$. Thus, for a mixture of scattering states at energy ϵ , we have

$$\mathbf{j} = \int d\mathbf{P} \rho(\mathbf{P}; \epsilon) \mathbf{j}[\psi(\mathbf{P})], \quad (28)$$

where $\rho(\mathbf{P}; \epsilon)$ are the diagonal elements of the density matrix describing the distribution of states within the circle of admissible in-plane momenta and $\psi(\mathbf{P})$ are scattering states corresponding to the in-plane momentum $\mathbf{P}$. Behind the barrier, the current is carried by the outgoing states only and, therefore, separating contributions stemming from different helicities we obtain

$$\begin{aligned} \mathbf{j} &= - \sum_\xi \xi \int d\mathbf{P} \rho(\mathbf{P}; \epsilon) |t_\xi(\mathbf{P})|^2 \left[\mathbf{h}_\xi^{(+)}(\mathbf{P}) \boldsymbol{\sigma} \left| \mathbf{h}_\xi^{(+)}(\mathbf{P}) \right| \right] \\ &= \sum_\xi \int d\mathbf{P} \rho(\mathbf{P}; \epsilon) |t_\xi(\mathbf{P})|^2 \mathbf{e}_\xi(\mathbf{P}), \end{aligned} \quad (29)$$

where $\mathbf{e}_\xi(\mathbf{P}) = -\xi \mathbf{h}_\xi^{(+)}(\mathbf{P}) / \tilde{\epsilon}_\xi$ [see Eq. (8)].

In order to discuss the main effect, we assume that the resonances corresponding to Klein tunneling are sufficiently narrow, so that we can approximate

$$\mathbf{j} = \rho_+(\mathbf{P}_+^{(K)}) \mathbf{e}_+(\mathbf{P}_+^{(K)}) + \rho_-(\mathbf{P}_-^{(K)}) \mathbf{e}_-(\mathbf{P}_-^{(K)}). \quad (30)$$

In other words, particles with different helicities flow along, generally speaking non-coinciding, directions specified by vectors

$$\mathbf{e}_\xi = \frac{1}{\epsilon} \left(k_\xi \mathbf{e}_x + \tilde{\mathbf{P}}_\xi^{(K)} \right), \quad (31)$$

where $\tilde{\mathbf{P}}_\xi^{(K)}$ is given by Eq. (23) with substituted $-\bar{\mathbf{A}} \rightarrow \Delta\mathbf{A}$ and $-\bar{\mathbf{q}} \rightarrow \Delta\mathbf{q}$.

The weight of contributions with different helicities is determined by the population of states with in-plane momenta corresponding to Klein tunneling. These momenta, in turn, can be controlled by external field in such way that the region of admissible

in-plane momenta may contain the resonant momentum only for one helicity. This effectively cancels the contribution of another helicity into outgoing current, making the current helicity-polarized. It must be noted that removal of the resonant momentum from the circle of admissible momenta does not imply that there are no propagating modes with the respective helicity at energy ϵ but rather signifies strong reflection of electrons with blocked helicity from the barrier.

5. Conclusion

An important feature distinguishing Weyl semimetals (WSM) from other Dirac materials is the separation between Weyl points with different chiralities. From the dynamical point of view, this introduces a matrix potential, each own for states with different helicities. When the separation is only in energy, the potential becomes purely scalar, while in the case of the separation only in the momentum space, the potential is vector. These potentials induce non-coinciding dynamics of states with different helicities. This provides opportunities to control the spatial flow of helicities in the *absence* of an external field acting directly on helicity.

We demonstrate the above property of WSM by considering transport properties of a multilayer Weyl semimetal structure formed by piece-wise constant potentials and separations between the Weyl points. In the case when there are no parallel electric and magnetic fields, so that the helicity fully conserves, there are two physical mechanisms discriminating between helicities. One is due to the dependence of the edge of the band on helicity. As a result, there are (direction dependent) energy regions, where the transmitted state is due to propagating modes inside the barrier for one helicity and due to tunneling for the opposite one.

We have shown, that the Klein tunneling provides additional mechanism of helicity selection. Using the formalism of spinor transfer matrices, we have found that there are directions, generally speaking helicity dependent, along which the electron propagates through the barrier with certainty regardless the width of the barrier. Near such resonance direction, the transmission regarded as a function of the in-plane momentum for a fixed energy is shown to be approximately of a Lorentzian form. Thus, when the directions of Klein tunneling for different helicities are well separated comparing to the width of the transmission resonance, the outgoing states are characterized by a strong helicity mismatch.

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Electronic and optical properties of vacancy defects in single-layer transition metal dichalcogenidesM. A. Khan,^{1,2} Mikhail Erementchouk,^{1,3} Joshua Hendrickson,⁴ and Michael N. Leuenberger¹¹*NanoScience Technology Center, Department of Physics, and College of Optics and Photonics,
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A detailed first-principles study has been performed to evaluate the electronic and optical properties of single-layer (SL) transition metal dichalcogenides (TMDCs) (MX_2 ; M = transition metal such as Mo, W, and $X = S, Se, Te$), in the presence of vacancy defects (VDs). Defects usually play an important role in tailoring electronic, optical, and magnetic properties of semiconductors. We consider three types of VDs in SL TMDCs: (i) X vacancy, (ii) X_2 vacancy, and (iii) M vacancy. We show that VDs lead to localized defect states (LDS) in the band structure, which in turn gives rise to sharp transitions in in-plane and out-of-plane optical susceptibilities, $\chi_{\parallel}$ and $\chi_{\perp}$. The effects of spin-orbit coupling (SOC) are also considered. We find that SOC splitting in LDS is directly related to the atomic number of the transition metal atoms. Apart from electronic and optical properties we also find magnetic signatures (local magnetic moment of $\sim \mu_B$) in $MoSe_2$ in the presence of the Mo vacancy, which breaks the time-reversal symmetry and therefore lifts the Kramers degeneracy. We show that a simple qualitative tight-binding model (TBM), involving only the hopping between atoms surrounding the vacancy with an on-site SOC term, is sufficient to capture the essential features of LDS. In addition, the existence of the LDS can be understood from the solution of the two-dimensional Dirac Hamiltonian by employing infinite mass boundary conditions. In order to provide a clear description of the optical absorption spectra, we use group theory to derive the optical selection rules between LDS for both $\chi_{\parallel}$ and $\chi_{\perp}$.

DOI: [10.1103/PhysRevB.95.245435](https://doi.org/10.1103/PhysRevB.95.245435)**I. INTRODUCTION**

Single-layer (SL) transition metal dichalcogenides (TMDCs) have attracted a lot of attention due to their intriguing electronic and optical properties, with a wide range of promising applications [1,2]. SL TMDCs are direct-band-gap semiconductors [3,4], which can be used to produce smaller and more energy efficient devices, such as transistors and integrated circuits. Moreover, the band gap lies in the visible region, which makes them highly responsive when exposed to visible light, a property with potential applications in optical detection. In contrast to graphene, SL TMDCs exhibit large intrinsic spin-orbit coupling (SOC), originating from the d orbitals of transition metal atoms. The presence of considerably high SOC (up to few hundred meV) [5–7] makes them a candidate material for exploring spin physics and spintronics applications.

Wafer-scale production of SL TMDCs is required to fully appreciate their technological potential. The most common experimental techniques used to produce large chunks of SL MoS_2 are (i) mechanical exfoliation, (ii) chemical vapor deposition, and (iii) physical vapor deposition. It has been observed that samples produced by all of these techniques have considerably lower carrier mobility than the theoretically predicted values [8,9]. It has recently been suggested that this discrepancy between the predicted and observed values of carrier mobility is due to the presence of impurities created during the growth process [10,11]. The most common and energetically favorable types of impurities are vacancy defects (VDs) [12]. Defects usually play an important role in tailoring various electronic and optical properties of two-dimensional materials and have been the subject of intense research over the last few decades.

VDs in semiconductors act as trapping centers for charge carriers and their interaction with charge carriers becomes stronger at reduced dimensionalities. Point defects in SL TMDCs have been explored both theoretically and experimentally [13–18]. Recent photoluminescence (PL) experiments [16–18] reveal that localized excitonic states related to VDs can serve as single-photon emitters in WSe_2 . Magnetism in low-dimensional systems is another area of interest [19,20]. It has been shown [21] that certain localized defect states (LDS) related to VDs can induce ferromagnetism in SL TMDCs, suggesting that they could be good candidates for spin channels in spintronic devices. In addition, LDS can be used to open and tune a band gap in graphene [22] and SL MoS_2 [23,24]. Various atomic defects can be realized artificially by using different experimental techniques. It has been shown that hexagonal pits ($3 \times MoS_2$) can be removed through etching of MoS_2 crystals by using XeF_2 as a gaseous reactant [23]. Point defects can be induced by irradiating the SL TMDCs with α particles or by thermal annealing [25]. Several experimental studies have been reported regarding the effects of point defects or of grain boundaries on SL TMDCs [26–28]. Strong PL enhancement has been observed as a result of oxygen adsorption at sulfur vacancy sites [27]. Also, sulfur vacancies are observed in MoS_2 through transmission electron microscopy experiments [28].

Pristine TMDCs are invariant with respect to the reflection σ_h about the Mo or W plane of atoms ($z = 0$ plane). Therefore, electron states can be classified into two categories: even and odd or symmetric and antisymmetric with respect to the $z = 0$ plane. We found that the even and odd bands in TMDCs have two different band gaps, $E_{g\parallel}$ and $E_{g\perp}$, respectively [29]. $E_{g\perp}$

TABLE I. Calculated in-plane and out-of-plane band gaps $E_{g\parallel}$ and $E_{g\perp}$ and spin-orbit splitting Δ_{SO} of the highest occupied valence band at K point.

System	MoS ₂	WS ₂	MoSe ₂	WSe ₂
$E_{g\parallel}$ [eV]	1.716	1.684	1.438	1.37
$E_{g\perp}$ [eV]	3.109	3.263	2.516	2.66
Δ_{SO} [meV]	150	438	195	482

has been usually neglected for pristine TMDCs because of its substantially larger value (Table I) and weak optical response [Fig. 2(b)] as compared with $E_{g\parallel}$. Earlier studies [24,29] show that the presence of VDs gives rise to LDS, in addition to the normal extended states present in conduction or valence bands in SL MoS₂. These LDS appear within the band-gap region and they can also be present deep inside the valence band, depending on the type of VD. Optical transitions between LDS across the Fermi level appear as resonance peaks, both in $\chi_{\parallel}$ and $\chi_{\perp}$, which shows that odd states are necessary for understanding the properties of VDs in SL MoS₂ [29].

In this paper, our aim is fourfold. First, we provide a comprehensive study of VDs in four types of SL TMDC materials: MoS₂, MoSe₂, WS₂, and WSe₂. Second, we provide detailed analytical models about the description of LDS within the Dirac equation formulation and by using the tight-binding model. Third, we include the effects of SOC on VDs, which has not been considered so far. As mentioned earlier, SOC in these materials is large and therefore needs to be taken into account in order to obtain a better understanding of the electronic and optical properties of TMDCs. Fourth, we briefly discuss defect-induced magnetism in some cases. Throughout this work, we consider three types of VDs: (i) single X vacancy, (ii) X_2 vacancy, and (iii) M vacancy.

This paper is organized as follows. Section II describes the numerical results obtained for band structures. Sections III and IV describe qualitative models for the existence of defected states. Section V deals with the optical response of defected SL TMDCs.

II. BAND STRUCTURE

The model system consists of a periodic two-dimensional (2D) superlattice of TMDCs [Figs. 1(a)–1(c)]. All numerical calculations are carried out using density functional theory (DFT). The local density approximation (LDA) is used

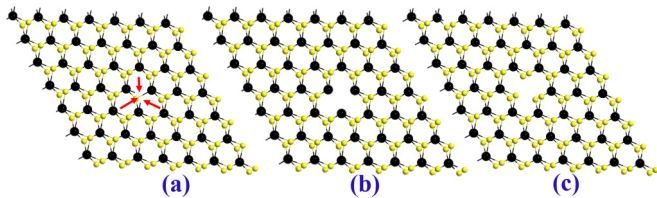


FIG. 1. Different types of vacancy defects. Yellow sphere is X while blue sphere is M : (a) X vacancy in a $7 \times 7 \times 1$ supercell, (b) X_2 vacancy consisting of a pair of X atoms (surrounded by M atoms) removed in a $7 \times 7 \times 1$ supercell, and (c) M vacancy (surrounded by X atoms) in a $7 \times 7 \times 1$ supercell.

with the Perdew-Zunger (PZ) parametrization [30] of the correlation energy of a homogeneous electron gas calculated by Ceperley-Alder [31]. The calculations are implemented within ATOMISTIX TOOLKIT 2015.1 [32] in order to be able to perform DFT calculations on large supercells in a reasonable amount of time. The periodic structure of the superlattice allows one to characterize the electron states by the band structure $\epsilon_n(\mathbf{k})$, where $\mathbf{k}$ is the vector in the first Brillouin zone of the superlattice and n enumerates different bands. We consider a $7 \times 7 \times 1$ (Fig. 1) supercell having 147 number of atoms with an edge length of 21.354 Å. The Brillouin zone of the supercell is sampled by a $3 \times 3 \times 1$ k -mesh. All the structures are geometrically optimized with a force tolerance of 0.05 eV/Å. SOC is taken into account via the norm-conserving pseudopotentials [33,34]. Band structures are calculated along the $\Gamma - M - K - \Gamma$ path. Band structures of SL TMDCs for the pristine cases are plotted in Fig. 2 and calculated values are given in Table I. The results are in good agreement with previously reported values both for band-gap and SOC energy [5,6,35,36]. We consider LDA because it is computationally less expensive and therefore allows us to perform DFT calculations on large supercells. A drawback of the generalized gradient approximation (GGA) is that the Atomistix Toolkit 2015.1 gives rise to an indirect band gap for SL TMDCs, which is in contradiction to the already established results for TMDCs. Nonetheless, we obtain approximately the same values for both the band gap and SOC using either LDA or GGA. Figures 3 and 4 show the band structure of various SL TMDCs in the presence of vacancies. The black lines denote regular electronic states within the valence or conduction bands while colored lines denote the LDS. Vertical arrows show some of the allowed optical transitions observed in the optical spectra (see Fig. 5).

III. TIGHT-BINDING MODEL AND SYMMETRIES

A. General considerations

The simplest qualitative model that can explain the existence of LDS in the band structure due to VDs is the tight-binding model (TBM). Within the TBM approximation the electron wave function can be presented as $|\psi\rangle = \sum_{j,\mu \in O_j} \psi_{\mu}^{(j)} \varphi_{\mu}^{(j)}(\mathbf{r} - \mathbf{R}^{(j)})$, where j enumerates atomic positions surrounding the vacancy and μ runs over the atomic orbitals O_j . In our tight-binding analysis only the atoms surrounding the VD are considered in order to make the calculations simple enough for capturing the essential physical properties of the problem. The three VDs can be classified into two groups on the basis of symmetries. The X vacancy lacks spatial inversion symmetry with respect to the M plane of atoms, i.e., the σ_h symmetry is broken and is therefore described by the group C_{3v} . In contrast, the X_2 and M vacancy preserve the σ_h symmetry of the crystal and thus can be described by the group D_{3h} [7,37]. For the latter the electronic states break down into even and odd parity with respect to the $\sigma_h : z \mapsto -z$ symmetry. d -orbitals of the transition metal and $p^{(t,b)}$ - orbitals (t and b denoting the top and bottom layers) of the chalcogen atoms give the largest contribution to the conduction and valence band structure of TMDC [35,38]. Based on the σ_h symmetry, the even and odd atomic orbitals are spanned by the

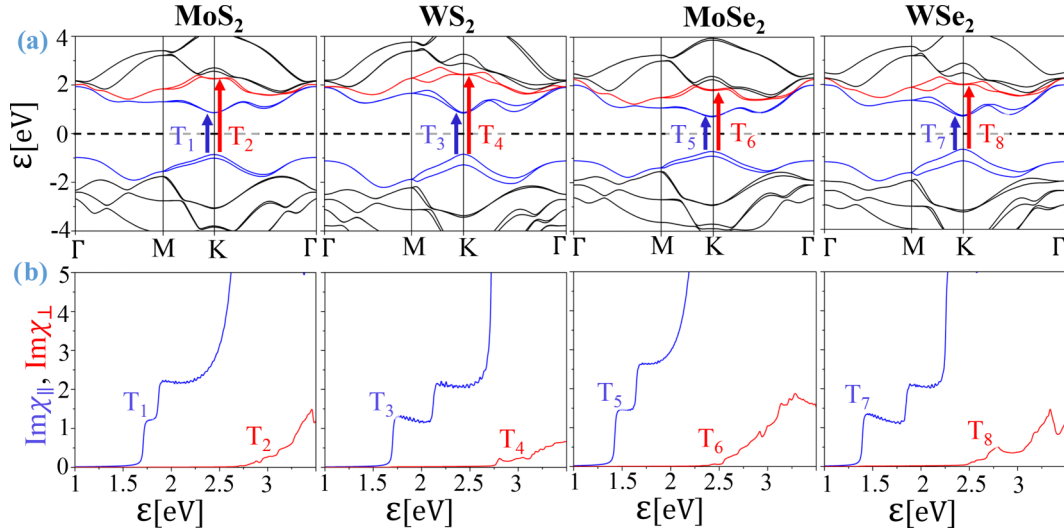


FIG. 2. (a) Band structures and (b) electrical susceptibility of pristine MX_2 monolayers. Band gaps $E_g^\parallel$ (blue), $E_g^\perp$ (red), and spin-orbit splitting Δ_{SO} in the valance band are given in Table I. Spin splitting can also be seen in the diagonal electric susceptibility in the in-plane component $\text{Im}(\chi_\parallel)$.

bases $\{d_{x^2-y^2}, d_{xy}, d_{z^2}, p_{x,y}^e = (p_{x,y}^{(t)} + p_{x,y}^{(b)})/\sqrt{2}, p_z^e = (p_z^{(t)} - p_z^{(b)})/\sqrt{2}\}$ and $\{d_{xz}, d_{yz}, p_{x,y}^o = (p_{x,y}^{(t)} - p_{x,y}^{(b)})/\sqrt{2}, p_z^o = (p_z^{(t)} + p_z^{(b)})/\sqrt{2}\}$, respectively. We also include the effects of intrinsic SOC of the form $\sim \mathbf{L} \cdot \mathbf{S}$. The resulting spin-orbit states transform according to irreducible representations (IRs) of the double groups C_{3v}^D and D_{3h}^D . Group representation theory is an efficient tool for determining the allowed optical transitions across the Fermi level in solids. This will be discussed in detail in the last section. The aim of this section is to present a qualitative description of LDS appearing in the band structure [Figs. 2(b)–2(d)]. Here, following Refs. [[6,29,38]] we first develop the TBM Hamiltonian by allowing the hopping between atomic orbitals of the atoms surrounding the VD only. Also, we consider a large supercell in order to suppress the intervacancy couplings. Consequently, the effects of SOC are considered as VD on-site couplings.

B. X and X_2 vacancy

Both X and X_2 vacancies are surrounded by three M atoms, as shown in Fig. 6. As mentioned earlier for M atoms, d orbitals provide the main contribution. Considering three atomic sites A, B, C with five d orbitals on each site, we have 15 species of d electrons. We will suppress the spin indices and denote electron operators collectively as a vector by $\psi = (\psi_1, \psi_2, \psi_3, \psi_4, \psi_5)$, with $\psi_\tau = (d_\tau^A, d_\tau^B, d_\tau^C)$, where d_τ^P denotes the annihilation operator of electrons for orbital τ at site P with $\tau = 1, 2, 3, 4, 5$ standing for $d_{z^2}, d_{xy}, d_{x^2-y^2}, d_{xz}, d_{yz}$, respectively. The spinless representation of the Hamiltonian can be expressed in block form as

$$\hat{H}_{X_2}^{TBM} = \begin{pmatrix} \hat{H}_e^{X_2} & \hat{0}_{9 \times 6} \\ \hat{0}_{6 \times 9} & \hat{H}_o^{X_2} \end{pmatrix}, \quad (1)$$

where $\hat{H}_e^{X_2}$ and $\hat{H}_o^{X_2}$ are 9×9 and 6×6 blocks with even (e) and odd (o) parity, with respect to σ_h , and

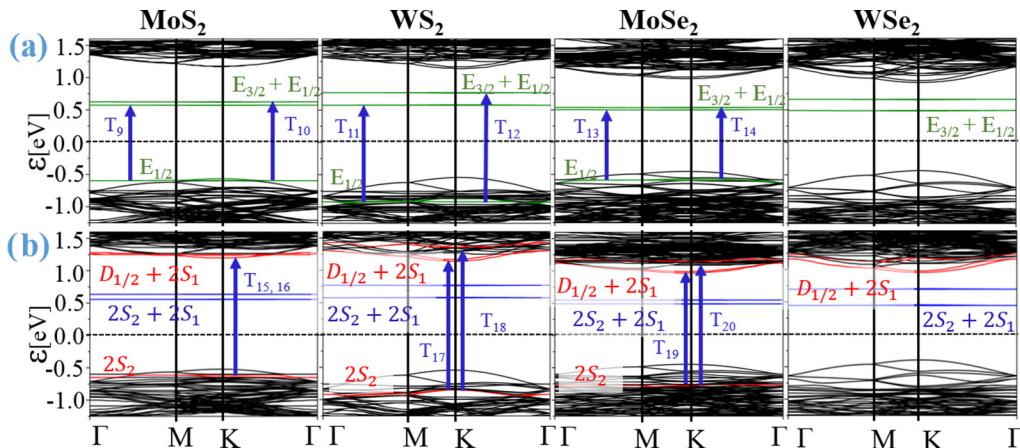


FIG. 3. Band structures of $7 \times 7 \times 1$ MX_2 SL TMDCs with X vacancy (a) and X_2 vacancy (b). The Fermi level is set at $\epsilon_F = 0$ eV. Red (blue) horizontal lines show odd (even) states with regard to σ_h , while green horizontal lines in (a) represent the states with no definite symmetry. Different LDS transform according to IRs $D_{1/2}$, $2S_2$, and $2S_1$ ($E_{1/2}$ and $E_{3/2}$) of the double group D_{3h}^D (C_{3v}^D).

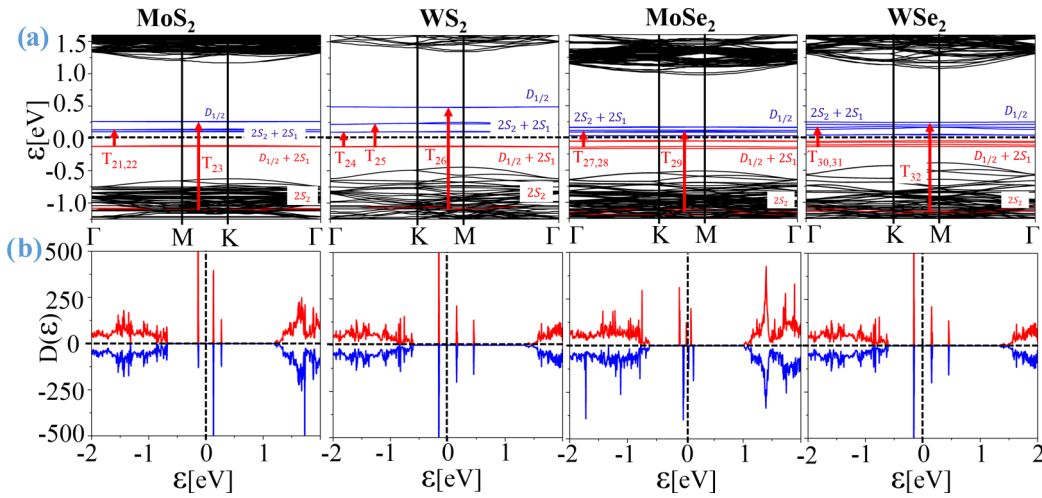


FIG. 4. (a) Band structures of $7 \times 7 \times 1$ MX_2 SL TMDCs with M vacancy. The Fermi level is set at $\epsilon_F = 0$ eV. Red (blue) lines show odd (even) states with respect to σ_h . Different LDS transform according to IRs $D_{1/2}$, $2S_2$, and $2S_1$ of double group D_{3h}^D . (b) Spin-polarized density of states of $7 \times 7 \times 1$ MX_2 SL TMDCs with M vacancy for spin-up (down) are shown in red (blue).

$\hat{0}_{m \times n}$ denotes a zero matrix of dimension $m \times n$. Here we take advantage of the inversion symmetry σ_h by decoupling the orbitals with opposite parities. Also, orthogonality between different orbitals on the same atomic site is enforced. The submatrices in Eq. (1) are given by

$$\hat{H}_e^{X_2} = \begin{pmatrix} \hat{H}_e^{1,1} & \hat{H}_e^{1,2} & \hat{H}_e^{1,3} \\ \hat{H}_e^{2,1} & \hat{H}_e^{2,2} & \hat{H}_e^{2,3} \\ \hat{H}_e^{3,1} & \hat{H}_e^{3,2} & \hat{H}_e^{3,3} \end{pmatrix}, \quad \hat{H}_o^{X_2} = \begin{pmatrix} \hat{H}_o^{4,4} & \hat{H}_o^{4,5} \\ \hat{H}_o^{5,4} & \hat{H}_o^{5,5} \end{pmatrix}, \quad (2)$$

where each of $\hat{H}_{e(o)}^{i,j}$ is a 3×3 matrix $i, j = 1, 2, 3, 4, 5$. The blocks in the above Hamiltonians read

$$\hat{H}_{e(o)}^{\alpha,\beta} = \begin{pmatrix} \epsilon_{e(o)}^{\alpha,\beta} & t_{e(o)}^{\alpha,\beta} e^{i\theta} & t_{e(o)}^{\alpha,\beta} e^{-i\theta} \\ t_{e(o)}^{\alpha,\beta} e^{-i\theta} & \epsilon_{e(o)}^{\alpha,\beta} & t_{e(o)}^{\alpha,\beta} e^{i\theta} \\ t_{e(o)}^{\alpha,\beta} e^{i\theta} & t_{e(o)}^{\alpha,\beta} e^{-i\theta} & \epsilon_{e(o)}^{\alpha,\beta} \end{pmatrix}. \quad (3)$$

The diagonal elements $\epsilon_{e(o)}^{\alpha,\beta}$ (0 for $\alpha \neq \beta$) and the off-diagonal elements $t_{e(o)}^{\alpha,\beta}$ are phenomenological parameters describing the on-site energy and hopping between d orbitals at different atomic sites, respectively. It can be easily shown that Hamiltonian (3) is invariant under σ_h and C_3 symmetry operations,

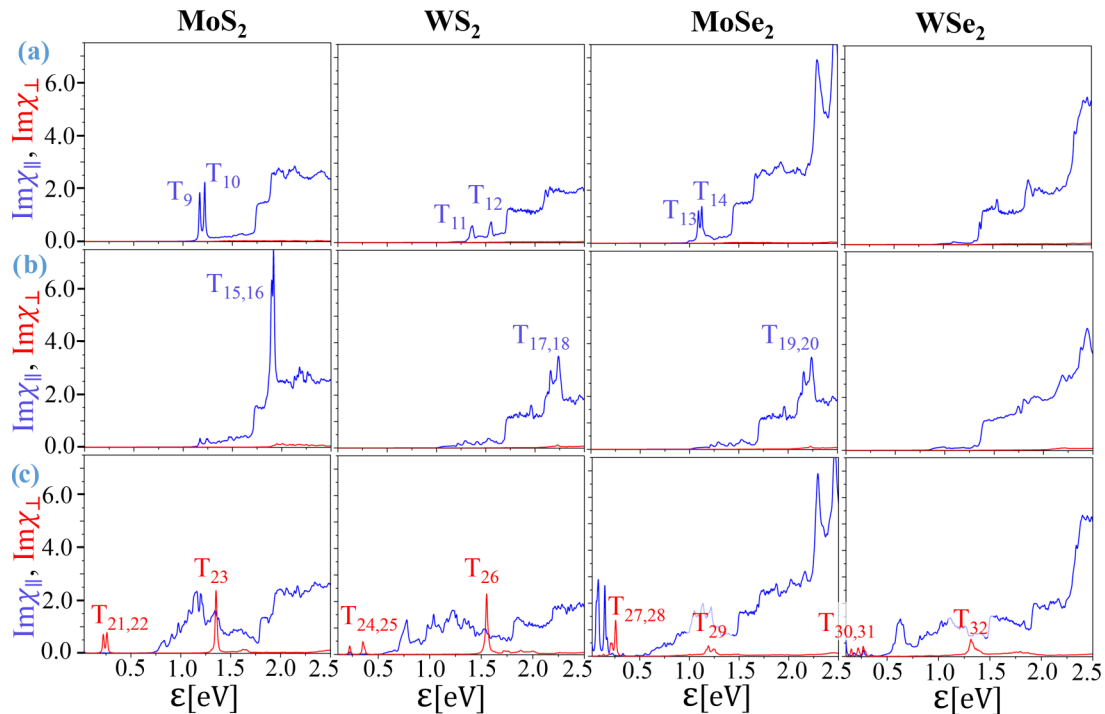


FIG. 5. Resonances of $\text{Im}\chi_{\parallel}(\omega)$ (blue) and $\text{Im}\chi_{\perp}(\omega)$ (red) (a) for X vacancy, (b) X_2 vacancy, and (c) M vacancy for different TMDCs.

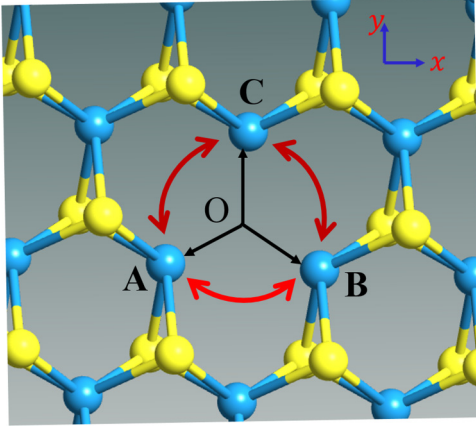


FIG. 6. X_2 vacancy surrounded by M atoms at atomic sites A, B, and C. The defect has a rotational symmetry at angles $2\pi/3$ (or $4\pi/3$) along the z axis passing through O .

for $\theta = 0, \pm 2\pi/3$. But, in addition to σ_h and C_3 symmetry operations, the D_{3h} group also contains σ_v symmetry operations, i.e., reflection by the planes perpendicular to the xy plane and passing through the lines OA, OB, and OC (Fig. 6). σ_v demands all the complex factors appearing in Eq. (3) to be 1 or equivalently, $\theta = 0$. Equations (2) and (3) provide an initial insight into the nature of LDS. One can easily show that, e.g., the $\hat{H}_o^{X_2}$ has a pair of three eigenvalues, i.e., $\bar{\epsilon} + t - \sqrt{(\delta\epsilon + h)^2 + 4t_h^2}$, $\bar{\epsilon} - t/2 - \sqrt{(\delta\epsilon - h/2)^2 + t_h^2}$, $\bar{\epsilon} - t/2 - \sqrt{(\delta\epsilon - h/2)^2 + t_h^2}$ and $\bar{\epsilon} + t + \sqrt{(\delta\epsilon + h)^2 + 4t_h^2}$, $\bar{\epsilon} - t/2 + \sqrt{(\delta\epsilon - h/2)^2 + t_h^2}$, $\bar{\epsilon} + t/2 - \sqrt{(\delta\epsilon - h/2)^2 + t_h^2}$, where $\bar{\epsilon}$, $\delta\epsilon$ are related to addition and subtraction of on-site energies for orbitals d_{xz} , d_{yz} ; t , h are related to addition and subtraction of hopping parameters of the same orbitals at different sites; and t_h is the hopping parameter of different orbitals at different atomic sites. Each pair contains a twofold doublet, which explains the existence of triplets within the band structure [29]. However, the apparent twofold degeneracy, which arises from the overlap of neighboring atomic orbitals, is lifted in the presence of SOC. Here we emphasize that each d orbital appears in the form of triplets in the band structure. Thus, there is a total of 15 LDS (in the absence of SOC) for the case of the X_2 vacancy. It may appear that the simplest TBM may contradict the numerical results in Fig. 3, where calculations show a lower number of LDS. A closer inspection of the numerical results, however, resolves this contradiction in favor of the TBM. In fact, in addition to the LDS appearing within the band-gap region, there are also LDS deep inside the valence bands, with a possibility to mix with the extended states in the bulk.

SOC in the Hamiltonian is included by a pure atomic term [6], and for simplicity we consider only the on-site contribution arising from the M atoms surrounding the vacancy. Using the basis $|d_{z^2}, \uparrow\rangle, |d_{xy}, \uparrow\rangle, |d_{x^2-y^2}, \uparrow\rangle, |d_{xz}, \uparrow\rangle, |d_{yz}, \uparrow\rangle$ and $|d_{z^2}, \downarrow\rangle, |d_{xy}, \downarrow\rangle, |d_{x^2-y^2}, \downarrow\rangle, |d_{xz}, \downarrow\rangle, |d_{yz}, \downarrow\rangle$, we can write the SOC Hamiltonian as

$$\hat{H}_{X_2}^{SOC} = \frac{\Delta}{2} \mathbf{L} \cdot \mathbf{S} = \frac{\Delta}{2} \begin{pmatrix} \hat{L}_z & \hat{L}_- \\ \hat{L}_+ & -\hat{L}_z \end{pmatrix}, \quad (4)$$

where

$$\hat{L}_z = \begin{pmatrix} \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 \\ \hat{0}_3 & \hat{0}_3 & 2i \times \hat{I}_3 & \hat{0}_3 & \hat{0}_3 \\ \hat{0}_3 & -2i \times \hat{I}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 \\ \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & -i \times \hat{I}_3 \\ \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & i \times \hat{I}_3 & \hat{0}_3 \end{pmatrix}, \quad (5)$$

$$\hat{L}_+ = \begin{pmatrix} \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \sqrt{3} \times \hat{I}_3 & i\sqrt{3}\hat{I}_3 \\ \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & -i \times \hat{I}_3 & -1 \times \hat{I}_3 \\ \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & -1 \times \hat{I}_3 & i \times \hat{I}_3 \\ -\sqrt{3} \times \hat{I}_3 & i \times \hat{I}_3 & \hat{I}_3 & \hat{0}_3 & \hat{0}_3 \\ -i\sqrt{3} \times \hat{I}_3 & \hat{I}_3 & -i \times \hat{I}_3 & \hat{0}_3 & \hat{0}_3 \end{pmatrix}, \quad (6)$$

and $\hat{L}_- = \hat{L}_+^\dagger$. The off-diagonal elements $\hat{L}_\pm$ in Eq. (4) couple the even to the odd blocks of the Hamiltonian matrix shown in Eq. (1) and are related to the spin-flip processes due to the SOC, which give rise to virtual transitions [39]. Because of the large spatial anisotropy of an atomically thin layer of TMDC, for the pristine case these off-diagonal terms can be neglected, which is substantiated by our DFT calculations (see below). A generalized SOC state has the form

$$|\Psi\rangle = \alpha|\zeta\rangle|\uparrow\rangle + \beta|\xi\rangle|\downarrow\rangle. \quad (7)$$

Here, $|\zeta\rangle$ and $|\xi\rangle$ are orbital states of the spin-up and spin-down states $|\uparrow\rangle$ and $|\downarrow\rangle$, respectively, and α , β are probability amplitudes for the up and down spinors. DFT calculations reveal that for SOC Bloch states corresponding to LDS, either $\alpha \ll \beta$ or $\alpha \gg \beta$ in the majority of cases (Fig. 7), corresponding to strong polarizations of the LDS in z direction (b), which is due to the large spatial anisotropy. It can be calculated that LDS are spin polarized for the X_2 vacancy or the Bloch states for the X_2 vacancy preserve the σ_h symmetry. Therefore we anticipate that the effects of $\hat{L}_\pm$ can safely be neglected for the X_2 vacancy. The full tight-binding Hamiltonian can be written as

$$\hat{H}_{X_2} = I_2 \otimes \hat{H}_{X_2}^{TBM} + \hat{H}_{X_2}^{SOC} \\ = \begin{pmatrix} \hat{H}_{X_2}^{TBM} + \frac{\Delta}{2} \hat{L}_z & \hat{0}_{9 \times 9} \\ \hat{0}_{9 \times 9} & \hat{H}_{X_2}^{TBM} - \frac{\Delta}{2} \hat{L}_z \end{pmatrix}. \quad (8)$$

The Hamiltonian appears to be block diagonal, which indicates that spin states in z direction are not mixed by spin-flip processes and therefore the spin in z direction is still a good quantum number due to σ_h symmetry. As mentioned above, the absence of spin-flip processes can be attributed to the 2D character of TMDCs or due to the large anisotropy between the xy plane and the z axis. In the case of the X vacancy, due to the lack of σ_h symmetry, defect states appear with no definite parity [Fig. 7(a)]. Therefore, here we argue that for the X vacancy the off-diagonal terms $\hat{L}_\pm$ in Eq. (4) need to be taken into account.

In the absence of SOC each energy band is doubly degenerate (spin-up and spin-down states at each K point). SOC lowers the symmetry and can break the spin degeneracy at K points away from the high-symmetry points. However,

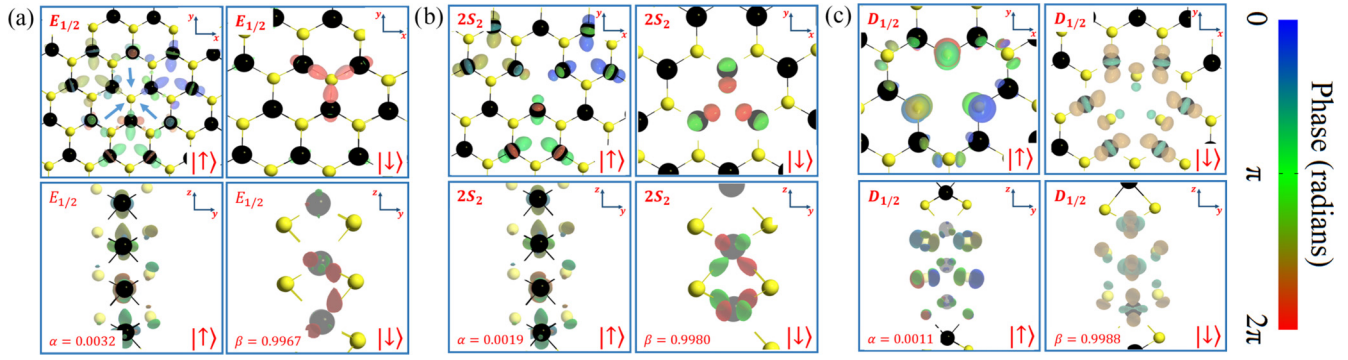


FIG. 7. Bloch states corresponding to a LDS: (a) X and (b) X_2 vacancy, and (c) M vacancy in MoS_2 . $E_{1/2}$ and $2S_2$ and $D_{1/2}$ are corresponding IRs. Both the top (xy plane) and side (yz plane) views are presented. Bloch states are spin polarized in each case $\beta \gg \alpha$.

time-reversal symmetry leads to the condition that $\varepsilon(\mathbf{k}, \uparrow) = \varepsilon(-\mathbf{k}, \downarrow)$, commonly known as Kramers degeneracy. This degeneracy is reflected in the band structure (Fig. 3), where each energy level is doubly degenerate for both types of vacancies. In solids or 2D surfaces spin splitting depends both on the size of atomic SOC and of the gradient of electric potential [40]. This difference in the gradient of electric potential leads to the different spin splittings for the same types of defects in different TMDCs, as shown in Fig. 3 and in Table II.

C. M vacancy

There are six chalcogen X atoms in the top and bottom layers, surrounding the transition metal M vacancy. Thus, there are 18 species of electrons corresponding to six possible combinations of p orbitals (three of them even and three odd with respect to σ_h) at three in-plane atomic positions. Proceeding as before the TBM for the M vacancy can be written as

$$\hat{H}_M^{TBM} = \begin{pmatrix} \hat{H}_e^M & \hat{0}_{9 \times 9} \\ \hat{0}_{9 \times 9} & \hat{H}_o^M \end{pmatrix}, \quad (9)$$

$$\hat{H}_e^M = \begin{pmatrix} \hat{H}_e^{6,6} & \hat{H}_e^{6,7} & \hat{H}_e^{6,8} \\ \hat{H}_e^{7,6} & \hat{H}_e^{7,7} & \hat{H}_e^{7,8} \\ \hat{H}_e^{8,6} & \hat{H}_e^{8,7} & \hat{H}_e^{8,8} \end{pmatrix}, \quad (10)$$

$$\hat{H}_o^M = \begin{pmatrix} \hat{H}_o^{9,9} & \hat{H}_o^{9,10} & \hat{H}_o^{9,11} \\ \hat{H}_o^{10,9} & \hat{H}_o^{10,10} & \hat{H}_o^{10,11} \\ \hat{H}_o^{11,9} & \hat{H}_o^{11,10} & \hat{H}_o^{11,11} \end{pmatrix}, \quad (11)$$

TABLE II. SOC splitting $\Delta_{X,X_2,M}$ in LDS appearing above the Fermi level for X , X_2 , and M vacancies, respectively, in different TMDCs.

System	MoS_2	WS_2	MoSe_2	WSe_2
Δ_X [meV]	51	192	34	173
Δ_{X_2} [meV]	78	278	60	251
Δ_M [meV]	32.5	130	54	100

where each $\hat{H}_{e(o)}^j$ is a 3×3 matrix corresponding to even (odd) combinations of p orbitals, with $j = 6, 7, 8, 9, 10, 11$ being indices reserved for the $p_x^e, p_y^e, p_z^e, p_x^o, p_y^o, p_z^o$ orbitals, respectively. Each $\hat{H}_{e(o)}^j$ in Eq. (10) has the same form as in Eq. (3).

SOC is included by considering the Hamiltonian described in Eq. (4). The M vacancy also preserves the σ_h symmetry. Again, the $\hat{L}_z S_z$ term gives the largest contribution due to the large anisotropy. The Bloch states are shown in Fig. 7, from which it can be concluded that LDS are spin polarized also in the case of M vacancy. The matrices for operators $\hat{L}_z$ and $\hat{L}_\pm$ in the case of the M vacancy can be written as

$$\hat{L}_z = \begin{pmatrix} \hat{0}_3 & -i \times \hat{I}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 \\ i \times \hat{I}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 \\ \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 \\ \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & -i \times \hat{I}_3 & \hat{0}_3 \\ \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & i \times \hat{I}_3 & \hat{0}_3 & \hat{0}_3 \\ \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 \end{pmatrix}, \quad (12)$$

$$\hat{L}_+ = \begin{pmatrix} \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & -1 \times \hat{I}_3 \\ \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & i \times \hat{I}_3 \\ \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{I}_3 & -i \times \hat{I}_3 & \hat{0}_3 \\ \hat{0}_3 & \hat{0}_3 & -1 \times \hat{I}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 \\ \hat{0}_3 & \hat{0}_3 & i \times \hat{I}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 \\ \hat{I}_3 & -i \times \hat{I}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 \end{pmatrix}, \quad (13)$$

and $\hat{L}_- = \hat{L}_+^\dagger$. The DFT calculations show that the Kramers degeneracy is preserved for MoS_2 and WS_2 , while it is broken for MoSe_2 and WSe_2 . In Ref. [21], it has been shown that the presence of Mo vacancies in MoSe_2 can induce spin polarization and results in long-range antiferromagnetic coupling between local magnetic moments, even at a distance above 13 Å, due to the large spatial extensions of spin density. The local magnetic moment on each M vacancy breaks the time-reversal symmetry and therefore lifts Kramers degeneracy in MoSe_2 in the presence of Mo vacancies. In

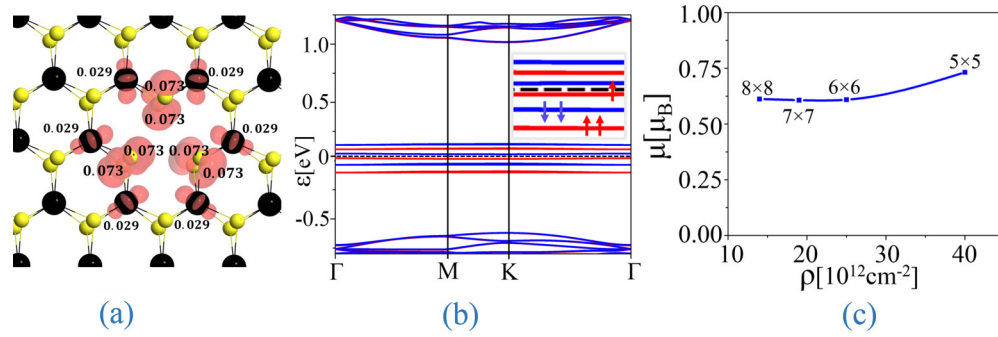


FIG. 8. (a) Isosurface plot of the spin density of MoSe₂ monolayer with one Mo vacancy. The black and yellow balls represent Mo and Se atoms, respectively. The red isosurface shows the spin density. The magnetic moment μ at neighboring and next-neighboring sites surrounding the vacancy is also calculated, which gives a total μ of 0.6 in units of μ_B . (b) Spin-polarized band structure of 7×7 MoSe₂ with one Mo vacancy, red and blue lines show states for spin-up and -down, respectively. (c) Magnetic moment μ vs defect density ρ .

Fig. 4(b) we show plots for the density of states (DOS) obtained by the local spin density approximation (LSDA) method for the M vacancy in different TMDCs in order to confirm that indeed the Mo vacancy in MoSe₂ exhibits magnetic signatures. Our spin-polarized DFT calculations show that the exchange correlation potential leads to a spin splitting only for the MoSe₂ system. In Fig. 8(a) the isosurface plot for the spin density is shown along with the magnetic moment μ calculated by means of the Mulliken population analysis at all the nearest-neighboring atomic sites (Se atoms) and the next-nearest-neighboring sites (Mo atoms) surrounding the vacancy. Our results show that the main contribution to the magnetism is due to the p orbitals localized at the Se atoms and the d orbitals localized at the next-nearest Mo atoms surrounding the Mo vacancy. The electronic band structure calculated by using LSDA is shown in Fig. 8(b). The spin states of the LDS are split, whereas the bulk states do not show any magnetic moment. The magnetic moment of the LDS is governed by the unpaired electron spins according to Hund's rules, which is $1 \mu_B$ [inset of Fig. 8(b)]. The calculations yield a slightly smaller magnetic moment of $0.6 \mu_B$, which is acceptable within standard DFT limits. Finally, we plot the magnetic moment μ vs defect density ρ in Fig. 8(c), where the localization of the magnetic moment is demonstrated for densities $\rho < 25 \times 10^{12} \text{ cm}^{-2}$. We also notice splittings in the case of WSe₂, but no magnetic signatures are found. We attribute this splitting as a result of interaction between adjacent vacancies due to large spatial extensions of W and Se orbitals.

IV. DEFECT STATES WITHIN THE DIRAC EQUATION FORMALISM

The main analytical tool for describing properties of electron states in transition metal monolayers is the Dirac equation, which emerges within the $k \cdot p$ approximation as the two-band model [5,41,42]. Such a description is valid when the main role is played by low-lying excitations near the band edges. This assumption, however, is ill justified for the case of vacancies and, indeed, as will be demonstrated below, the Dirac equation fails to reproduce many important features of the defect states. At the same time, the Dirac equation allows one to establish several important features and, first of all, the

sole existence of the states bound to vacancies. For example, within the framework provided by the Schrodinger equation, the vacancy is naturally represented by a repulsive potential that cannot support bound states. The Dirac equation, in turn, provides more options for describing defects and, as shown below, when the special boundary conditions are enforced at the boundary of the defect, the states localized near the boundary appear.

The formalism of the Dirac equation can be introduced as follows. Within the $k \cdot p$ approximation the electron states are described by $\Psi(\mathbf{r})e^{i\mathbf{K}\cdot\mathbf{r}}$, where $\Psi(\mathbf{r})$ is a smooth function of coordinates. Adopting the two-band approximation, $\Psi(\mathbf{r})$ is presented as a two-component spinor, which satisfies a 2D Dirac-like equation. For example, for MoS₂ the two-band approximation is often implemented retaining only the dominating contribution of Mo's d orbitals [5,6], so that near the inequivalent K points of the Brillouin zone, $\mathbf{K}_\tau = \tau \mathbf{K}$ with $\tau = \pm 1$, spinors $\Psi_\tau(\mathbf{r})$ are spanned by $|d_{x^2-y^2} - i\tau d_{xy}\rangle$ and $|d_{z^2}\rangle$, the states representing the top of the valence band and the bottom of the conduction band, respectively. Spinors Ψ_τ , thereby, satisfy $[\sigma_z \Delta + v(\tau \sigma_x p_x + \sigma_y p_y)]\Psi_\tau(\mathbf{r}) = \epsilon \Psi_\tau(\mathbf{r})$, where 2Δ is the width of the gap and ϵ is the energy counted from the center of the gap ϵ_c .

In order to eliminate the valley dependence of the Hamiltonian governing the spatial distribution of Ψ_τ , it is convenient to introduce $\Phi_+ = \Psi_+$ and $\Phi_- = \sigma_y \Psi_-$, which satisfy $\mathcal{H}_\tau \Phi_\tau = \epsilon \Phi_\tau$, where

$$\mathcal{H}_\tau = \tau \sigma_z \Delta + v \boldsymbol{\sigma} \cdot \mathbf{p}. \quad (14)$$

Thus solutions for electrons in different valleys are related by simply reverting the sign of Δ . Combining $\Phi_\pm$ into a single 4-spinor,

$$\Phi = \Phi_+ \oplus \Phi_-, \quad (15)$$

the equations of motion for different valleys can be presented in a unified form $\mathcal{H}\Phi = \epsilon\Phi$ with

$$\mathcal{H} = \tau_z \otimes \sigma_z \Delta + v \tau_0 \otimes \boldsymbol{\sigma} \cdot \mathbf{p}, \quad (16)$$

where τ_i with $i = x, y, z$ and τ_0 are the Pauli matrices and the identity matrix, respectively, acting on the valley space.

Hamiltonian (16) possesses the cylindrical symmetry, which can be employed by presenting $\boldsymbol{\sigma} \cdot \mathbf{p} = -i\sigma_r \partial/\partial r -$

$ir^{-1}\sigma_\phi\partial/\partial\phi$, where

$$\sigma_r = \begin{pmatrix} 0 & e^{-i\phi} \\ e^{i\phi} & 0 \end{pmatrix}, \quad \sigma_\phi = \begin{pmatrix} 0 & -ie^{-i\phi} \\ ie^{i\phi} & 0 \end{pmatrix}. \quad (17)$$

The explicit angular dependence is eliminated by introducing $\tilde{\Phi}_\tau = e^{i\sigma_z\phi/2}\Phi_\tau$, which accounts for rotation of the spinors Φ_τ while encircling the origin. It should be noted that due to the relation $\Phi_- = \sigma_y\Psi_-$, the rotation directions of Ψ_+ and Ψ_- are different: $\tilde{\Psi}_\tau = e^{i\tau\sigma_z\phi/2}\Psi_\tau$. Thus the winding numbers of spinors corresponding to electrons belonging to different valleys have opposite signs.

Spinors $\tilde{\Phi}_\tau$ satisfy

$$\tilde{\mathcal{H}}_\tau \tilde{\Phi}_\tau = \epsilon \tilde{\Phi}_\tau, \quad (18)$$

where $\tilde{\mathcal{H}}_\tau = e^{i\sigma_z\phi/2}\mathcal{H}_\tau e^{-i\sigma_z\phi/2}$ has the form

$$\tilde{\mathcal{H}} = \tau\sigma_z\Delta - iv\left[\sigma_x\left(\frac{\partial}{\partial r} + \frac{1}{2r}\right) + \sigma_y\frac{1}{r}\frac{\partial}{\partial\phi}\right]. \quad (19)$$

Equation (18) is solved by separating the variables $\tilde{\Phi}_\tau(r, \phi) = \sum_{m=-\infty}^{\infty} \tilde{\Phi}_{\tau,m}(r)e^{im\phi}$. For amplitudes $\tilde{\Phi}_{\tau,m}(r)$, we find the general solution

$$\tilde{\Phi}_{\tau,m}(r) = \sqrt{Qr} \times \left(\frac{1}{\sqrt{\epsilon-\tau\Delta}} [a_{\tau,m}h_{m-1}^{(1)}(Qr) + b_{\tau,m}h_{m-1}^{(2)}(Qr)] + \frac{i}{\sqrt{\epsilon+\tau\Delta}} [a_{\tau,m}h_m^{(1)}(Qr) + b_{\tau,m}h_m^{(2)}(Qr)] \right), \quad (20)$$

where $h_m^{(1,2)}(Qr)$ are the spherical Hankel functions, $Q = v^{-1}\sqrt{\Delta^2 - \epsilon^2}$, and $a_{\tau,m}, b_{\tau,m}$ are arbitrary constants.

We are interested in bound states and, therefore, in solutions of Eq. (18) corresponding to energies inside the gap. For such energies, we have $Q = i\kappa$ with non-negative $\kappa = \sqrt{\Delta^2 - \epsilon^2}$. From the regularity condition at infinity, it follows that $b_\tau^{(m)} = 0$, while $a_\tau^{(m)}$ are determined from the normalization condition. The solution can be written as

$$\tilde{\Phi}_{+,m} = N_{+,m} \begin{pmatrix} \frac{1}{\sqrt{\Delta-\epsilon}} g_{m-1}(\kappa r) \\ \frac{i}{\sqrt{\Delta+\epsilon}} g_m(\kappa r) \end{pmatrix}, \quad (21)$$

where we have denoted the normalization constant by $N_{+,m}$. The functions $g_m(z)$ are related to the modified spherical

Hankel functions $g_m(z) = 2k_m(z)/\pi$ and for $m > 0$ can be presented as

$$g_m(z) = (-z)^m \left(\frac{d}{zdz} \right)^m \frac{e^{-z}}{z}. \quad (22)$$

Taking into account the relation

$$g_{-m}(z) = g_{m-1}(z), \quad (23)$$

we can use Eq. (22) for finding $g_m(z)$ with $m < 0$ as well. With the help of this relation, one can show, starting from Eq. (20), that

$$\tilde{\Phi}_{-,-m} = c\sigma_x \tilde{\Phi}_{+,m}, \quad (24)$$

where c is a phase factor, $|c| = 1$. Such connection between solutions corresponding to electrons from different valleys allows us to limit our attention to $\tau = +1$.

The functions $g_m(z)$ can be shown to be non-negative. Thus, we can rewrite

$$\tilde{\Phi}_{+,m} = \tilde{N}_{+,m} \begin{pmatrix} \cos(\chi_m/2) \\ i \sin(\chi_m/2) \end{pmatrix}, \quad (25)$$

with $0 \leq \chi_m \leq \pi$. This representation shows that at any chosen distance from the center of the vacancy, the defect states have the form of a spin coherent state [43,44] lying in the plane perpendicular to $\mathbf{n}_B$, the vector normal to the boundary of the anti-dot and directed outward. The angle $\chi_m = 2 \arctan(F_m)$, where

$$F_m = \frac{g_m(\kappa r)\sqrt{\Delta-\epsilon}}{g_{m-1}(\kappa r)\sqrt{\Delta+\epsilon}}, \quad (26)$$

has the meaning of the polar angle of the vector characterizing the direction of the spin coherent state. Its dependence on m is illustrated by Fig. 9, which shows that χ_m monotonously increases from $\chi_{-\infty} = 0$ to $\chi_{\infty} = \pi$. It is also a monotonous function of r (increasing for $m < 0$ and decreasing for $m > 0$) and a monotonously increasing function of energy. Taking into account Eq. (23) one can see the important symmetry

$$F_m(\epsilon) = 1/F_{-m}(-\epsilon). \quad (27)$$

Thus, the states with $\tau = 1$ lie in the half plane corresponding to the positive projection on the vector tangent to the

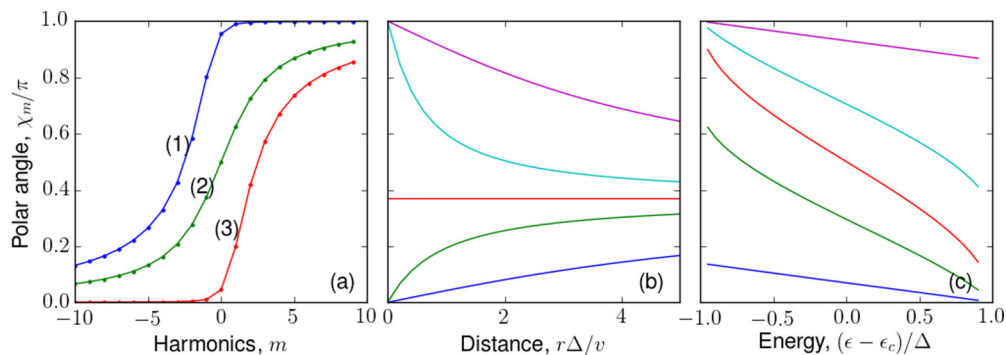


FIG. 9. The polar angle χ_m characterizing the defect state. (a) Dependence of χ_m on m . Curves (1), (2), and (3) correspond to $(\epsilon - \epsilon_c)/\Delta = -0.99, 0, 0.99$, respectively, where ϵ_c stands for the center of the gap. The distance from the center of the anti-dot is taken $r\Delta/v = 1$ (it is assumed that $r > r_0$). (b) For the fixed energy $(\epsilon - \epsilon_c)/\Delta = 0.4$ the dependence χ_m on r is shown for m ; from top to bottom $m = 5, 1, 0, -1, -5$. (c) For $r\Delta/v = 1$ the dependence of χ_m on energy is shown for the same set of m as in (b).

boundary $\mathbf{e}_\phi = \mathbf{e}_z \times \mathbf{n}_B$, while the states with $\tau = -1$ have the opposite orientation, due to $\langle \tilde{\Phi}_{-,m} | \tilde{\Phi}_{+,m} \rangle = 0$, which can be easily checked.

The energies of the defects states (and their sole existence) are determined by the boundary condition on the boundary of the anti-dot. The general form of the condition is found requiring that the radial component of the probability current must vanish at the boundary [45,46] $\langle \Phi(r_0) | \mathbf{n}_B \cdot \mathbf{J} | \Phi(r_0) \rangle = 0$, where $\mathbf{J} = v\tau_0 \otimes \boldsymbol{\sigma}$. This condition is equivalent to $M\Phi = \Phi$, where Φ is the 4-spinor defined by Eq. (15) and the Hermitian matrix M has the eigenvalues ± 1 and anticommutes with the radial component of the current operator $\{\mathbf{J} \cdot \mathbf{n}_B, M\} = 0$. Within the infinite mass model [45,46], the anti-dot is represented as a region with renormalized width of the gap $\Delta \rightarrow \Delta(1 + d(r))$, with $d(r) = 0$ for $r > r_0$ and $d(r) \rightarrow \infty$ when $r < r_0$, so that in this case $M = (\boldsymbol{\tau} \cdot \mathbf{e}_z) \otimes (\boldsymbol{\sigma} \cdot \mathbf{e}_\phi)$. In other words, within this model in order to have decaying electron distribution inside the anti-dot $\tilde{\Phi}_\tau(r)$ must be proportional to $|\tau \mathbf{e}_\phi\rangle$ as r approaches r_0 .

The condition $\tilde{\Phi}_{+,m}(r_0) \propto |\mathbf{e}_\phi\rangle$, or $\chi_m = \pi/2$, constitutes the condition imposed on the energy of the bound state:

$$F_m(\epsilon, r_0) = 1. \quad (28)$$

In virtue of Eq. (27), if for some m there exists a bound solution with the energy ϵ , then there is the solution corresponding to $m' = -m$ with the energy $-\epsilon$. Thus within the infinite mass model the spectrum of the defect states is symmetric with respect to the center of the gap.

For $m = 0$, Eq. (28) has the simplest form $F_0 = \sqrt{\Delta - \epsilon} / \sqrt{\Delta + \epsilon} = 1$ with the solution

$$\epsilon_0 = 0. \quad (29)$$

Thus the anti-dot independently of its size supports a bound state with the energy at the center of the gap.

States with $|m| > 0$, in turn, appear only when the defect is sufficiently large. In order to find the condition of supporting the state with some m we notice that $F_m(\epsilon, r_0)$ is a monotonously decreasing function of energy while ϵ changes from $-\Delta$ to Δ . Since $g_m(z \rightarrow 0) \approx (2m-1)!!/z^{m+1}$, we find that the energy of the m th state is inside the gap if

$$r_0 > R_m = \frac{v}{\Delta} \left(|m| - \frac{1}{2} \right). \quad (30)$$

Conversely, for the given radius r_0 the number of bound defect states is given by $N = 4 + 8[r_0\Delta/v + 1/2]$, where 4 accounts for states from different valleys and with different spins at $m = 0$ and the second term accounts for states with $m > 1$; here $[\dots]$ denotes taking the integer part and 8 in addition to the spin and valley degeneracies accounts for the symmetry $m \rightarrow -m$. The dependence of energies of the defect states on the radius of the anti-dot is shown in Fig. 10.

The spatial electron distribution corresponding to the defect state is conveniently characterized by the probability density $\rho_{\tau,m}(r) = \langle \Phi_{\tau,m} | \Phi_{\tau,m} \rangle$ and the vector of orientation of the (pseudo)spin coherent state $\mathbf{S}_{\tau,m} = \langle \Phi_{\tau,m} | \boldsymbol{\sigma} | \Phi_{\tau,m} \rangle / \rho_{\tau,m}$. As follows from Eq. (25), the pseudospin state is transversal, $S_r = 0$, with the spatial variation of the projection of $\mathbf{S}_{\tau,m}$ onto the $(\mathbf{e}_\phi, \mathbf{e}_z)$ plane depending on m .

In the simplest case $m = 0$ the pseudospin remains in the plane of the layer, $S_{\tau,z} = 0$. States with nonzero m

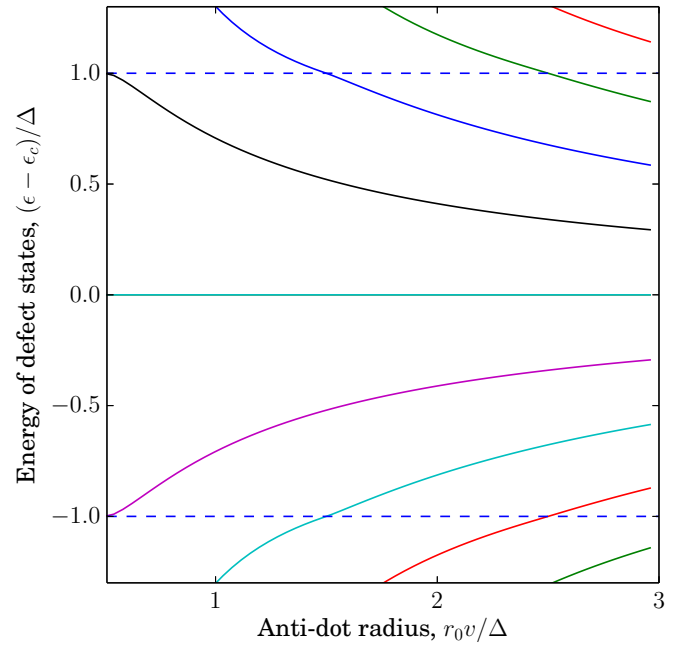


FIG. 10. The dependence of the spectrum of defect states on the normalized radius of the anti-dot, $r_0 v / \Delta$. The dashed lines show the edges of the gap. The section at particular r_0 presents the spectrum of the defect states in the infinite mass model. The central line corresponds to $m = 0$, and states with increasing $|\epsilon - \epsilon_c|$ correspond to states with increasing $|m|$. Thus curves for $m = -4, \dots, 4$ are shown. The spectral lines outside the gap correspond to scattering resonances with complex energies.

are characterized by the out-of-plane distribution of the pseudospin (for $r > r_0$). The angle of maximum deviation from the plane is

$$\tan\left(\frac{\beta}{2}\right) = \tau \frac{\sqrt{\Delta + \epsilon} - \sqrt{\Delta - \epsilon}}{\sqrt{\Delta + \epsilon} + \sqrt{\Delta - \epsilon}}. \quad (31)$$

Thus for $\tau = 1$ the pseudospin “sticks out” of the plane for $\epsilon > 0$ (that is for $m > 0$) and has the negative projection on the z axis for $\epsilon < 0$. For $\tau = -1$ the direction of the pseudospin is reversed.

V. OPTICAL RESPONSE

The presence of LDS in the band structure gives rise to sharp peaks in the optical spectrum. In Ref. [47] the relative dielectric functions ϵ_r of various TMDCs have been

TABLE III. Character table of the group C_{3v} . E , C_3 , σ_v are the single-group IRs and $E_{1/2}$, $E_{3/2}$ are the corresponding double-group IRs.

C_{3v}	E	C_3	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
$E_{1/2}$	2 - 2	1 - 1	0 0
$E_{3/2}$	2 - 2	-2 2	0 0

TABLE IV. Character table of the group D_{3h} . E , σ_h , $2C_3$, $2S_3$, $3C_2$, and σ_v are the single-group IRs, and $D_{1/2}$, $2S_1$, and $2S_2$ are the corresponding double-group IRs.

D_{3h}	E	σ_2	$2C_3$	$2S_3$	$3C_2$	$3\sigma_v$
A'_1	1	1	1	1	1	1
A'_2	1	1	1	1	-1	-1
A''_1	1	-1	1	-1	1	-1
A''_2	1	-1	1	-1	-1	1
E'	2	2	-1	-1	0	0
E''	2	-2	-1	1	0	0
$D_{1/2}$	2 - 2	0	1 - 1	$\sqrt{3}$ - $\sqrt{3}$	0	0
$2S_1$	2 - 2	0	-2 2	0 0	0	0
$2S_2$	2 - 2	0	1 - 1	$-\sqrt{3}$ $\sqrt{3}$	0	0

measured experimentally, which in turn are related to the electric susceptibilities by the standard formula $\epsilon_r = 1 + \chi$. In Fig. 5 results for both in-plane $\chi_{\parallel}$ and out-of-plane $\chi_{\perp}$ components of the electric susceptibility are presented for different VDs in TMDCs. The electric susceptibility provides valuable insight into the optical selection rules for transitions between states across the Fermi level. We are interested in transitions involving states with energy near the gap edges or inside the gap. The electric susceptibility tensor is evaluated using the Kubo-Greenwood formula,

$$\chi_{ij}(\omega) = -\frac{e^2 \hbar^4}{m^2 \epsilon_0 V \omega^2} \sum_{p,q} \frac{f(E_q) - f(E_p)}{E_{pq} - \hbar\omega - i\hbar\Gamma} \pi_{pq}^i \pi_{qp}^j, \quad (32)$$

where $\pi_{pq}^j = \langle \psi_p | x_j | \psi_q \rangle$ is the j th component of the dipole matrix element between states p and q , V the volume, f the Fermi function, and Γ is the broadening, which is set to be 0.01 eV. The appearance of states inside the band gap E_g or close to the band edges leads to the resonances at single energy $E_{pq} = |E_p - E_q|$. The dipole matrix element π_{pq}^j determines the strength of an optical transition and whether it is allowed or prohibited by symmetries.

When considering defects in a crystal, the LDS transform according to the IRs of the symmetry group of the crystal site in which the defect resides. While the translational symmetry of the crystal is broken, point-group symmetries are partially or completely preserved. M and X_2 vacancies keep the D_{3h} symmetry, whereas the X vacancy exhibits the lower C_{3v} symmetry. The character tables for C_{3v} and D_{3h} with single- and double-group IRs are shown in Tables III and IV, respectively. Table V contains the decomposition of the direct products of the single-group representations with the representation according to which the spin matrices transform, i.e., $E_{1/2}$ and $D_{1/2}$, respectively. In Fig. 11 band structures for WS_2 with S and W vacancies are shown with and without SOC. Following Refs. [48] and [49], in Fig. 11 we show how the single-group IRs in the absence of SOC can be mapped to the

corresponding double-group IRs in the presence of SOC. Note that due to the nature of the DFT calculation, the superlattice defined by the supercell introduces an artificial translational symmetry, which in some cases leads to artificial splittings. These can be typically recognized by systematically changing the size of the supercell.

The appearance of LDS inside the band gap leads to sharp resonances in $\chi_{\parallel}$ and $\chi_{\perp}$ at frequencies corresponding to the energy differences between LDS. However, not all transitions are allowed. Instead, several transitions are prohibited due to symmetry, i.e., when π_{pq}^j does not transform according to the symmetric representation of the symmetry group of the superlattice. In the matrix element χ_{pq}^j , the initial state ψ_p , the final state ψ_q , and the position operator x_j transform according to the IRs $\Gamma(\psi_p)$, $\Gamma(\psi_q)$, and $\Gamma(x_j)$, respectively. An electric dipole transition between two states is allowed if the direct product $\Gamma(\psi_p) \otimes \Gamma(x_j) \otimes \Gamma(\psi_q)$ includes $\Gamma(I)$ in its decomposition in terms of a direct sum. $\Gamma(I)$ denotes the IR for the identity, i.e., A_1 and A'_1 for C_{3v} and D_{3h} , respectively. This is strictly related to the polarization of the radiation. One needs to consider separately the in-plane and out-of-plane components of π_{pq}^j because they transform according to different IRs of C_{3v} and D_{3h} . The selection rules for electric dipole transitions for the double-group IRs are summarized in Table VI.

The presence of SOC couples the spin and orbital angular momenta, thereby requiring the consideration of the double-group IRs. In our case, we need to consider $D_{1/2} \otimes C_{3v}$ and $D_{1/2} \otimes D_{3h}$, where $D_{1/2}$ is the 2D spin representation. The electromagnetic field couples to the orbital part of the state, i.e., either to $|\zeta\rangle$ or to $|\xi\rangle$ [see Eq. (7)]; polarizations induced by electromagnetic waves will not be changed in the presence of SOC. The role of the SOC is to lift some degeneracies, which gives rise to extra absorption peaks compared with the case without SOC [29]. In the susceptibility, these extra peaks lie close to the energies predicted by the susceptibility without SOC. It is important to take care when dealing with selection rules described by double groups because double groups may allow some transitions that are prohibited by the single groups. Then such selection rules must be discarded. One such example is the π transition for the X vacancy. In the absence of SOC, the π transition is allowed only between states with the IRs E , i.e., $E \otimes A_1 \otimes E = A_1 \oplus A_2 \oplus E$; this transition is not allowed since orbitals of the IR E exist above the Fermi level only. In the presence of SOC the π transition is allowed by the double group, i.e., $E_{1/2} \otimes A_1 \otimes E_{3/2} = A_1 \oplus A_2 \oplus E$, but is not seen in the susceptibility including SOC. This can be understood as the artefact of double groups, since π transitions are prohibited in the absence of SOC.

As a final note, as mentioned earlier, all samples are geometrical optimized before performing electronic calculations. Geometrical optimization may break certain symmetries and

TABLE V. Double-group representations obtained from single-group representation for C_{3v} and D_{3h} .

$\Gamma_i(C_{3v})$	A_1	A_2	E	$\Gamma_i(D_{3h})$	A'_1	A'_2	A''_1	A''_2	E'	E''
$\Gamma_i \times E_{1/2}$	$E_{1/2}$	$E_{1/2}$	$E_{3/2} + E_{1/2}$	$\Gamma_i \times D_{1/2}$	$D_{1/2}$	$D_{1/2}$	$2S_2$	$2S_2$	$2S_1 + 2S_2$	$2S_1 + D_{1/2}$

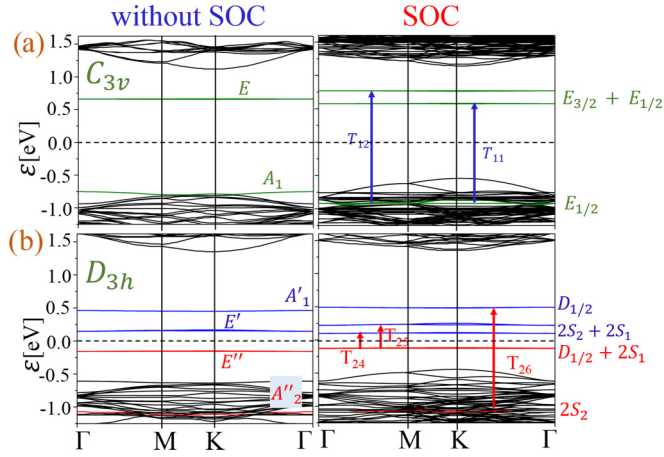


FIG. 11. Band structures without (a) and with SOC (b) for WS₂. The mapping of the LDS from the band structure without SOC to the band structure with SOC follows the mapping of the single-group IRs to the double-group IRs including spin, as explained in Table V.

can affect certain selection rules or can result in concealing of some of the resonances.

VI. CONCLUSION

In this paper we have provided numerical and analytical descriptions of electronic and optical properties of SL TMDCs in the presence of VDs. We have shown that the presence of LDS gives rise to sharp transitions both in $\chi_{\parallel}$ and $\chi_{\perp}$. In order to understand these transitions, odd states need to

TABLE VI. Electric dipole selection rules in C_{3v} and D_{3h} symmetry. σ represents in-plane transitions while π represents out-of-plane transitions.

C_{3v}	$E_{1/2}$	$E_{3/2}$	D_{3h}	$D_{1/2}$	$2S_1$	$2S_2$
$E_{1/2}$	σ, π	σ	$D_{1/2}$		σ	σ, π
$E_{3/2}$	σ	σ, π	$2S_1$	σ	π	σ
			$2S_2$	σ, π	σ	

be considered in addition to even states. A central result of our paper is that group theory can be used to derive strict selection rules for the optical transitions, which are in excellent agreement with the susceptibility calculated using the Kubo-Greenwood formula with the DFT orbitals. SOC-induced splitting is observed in LDS and is seen to be larger for VDs in WX₂ than in MoX₂. Interestingly, our findings suggest magnetic properties of MoSe₂ in the presence of Mo vacancy, which may be enhanced by increasing the density of defects. In order to provide a qualitative explanation of the existence of LDS, we performed analytical calculations based on the TBM and 2D Dirac formulation. All these results considerably improve the understanding of VDs in SL TMDCs and should benefit their potential applications in optoelectronic and nanoelectronic devices.

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Weyl fermions in cylindrical wires

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The key feature of Weyl semimetals (WSMs) is the presence of topologically protected Dirac cones in a three-dimensional material. We consider the effect of restricting geometry on the spectrum of excitations in WSMs using as a model a cylindrical WSM wire. For the full manifold of hard boundary conditions, we derive the general form of the dispersion equation relating the energy of the excitations and their momentum along the wire. We show that only the special class of boundary conditions, corresponding to decoupled helicities or, equivalently, to pinned directions of the electron spin on the surface, support massless excitations. For a general boundary condition, these excitations acquire mass inversely proportional to the radius of the wire. This demonstrates that boundary phenomena may play a crucial role in formation of excitations in WSM based structures.

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I. INTRODUCTION

Recent synthesis of Weyl semimetals (WSMs) [1–6] marks a significant achievement in a series of efforts invested in finding solid state implementations of Weyl materials, whose unique properties were envisioned almost a century ago [7]. The principal feature of the new emergent class of materials such as TaAs, NbAs is that they realize WSMs in stoichiometric single crystals rather than in a material with carefully crafted chemical composition as, for instance, in $Q\text{-Bi}_{1-x}\text{Sb}_x\text{Te}_3$ with $Q = \text{La}$ or Lu , where the WSM phase was expected for $0.39 < x < 0.42$ and $0.41 < x < 0.46$, respectively [8], or in a complex heterostructure as, for example, in HgTe/CdTe multilayers [9]. Owing to the relative simplicity of the discovered materials, WSMs started to leave the realm of theoretical high-energy physics and to attract significant attention from more “everyday” perspectives including possible applications of WSMs in a new type of electronics, weyltronics, based on unique features of WSMs [10,11]. The property that sets WSMs apart from other Dirac materials is the separation of Dirac points corresponding to states with different helicities, which provides means for dynamical distinction between such states. This property of WSMs is a subject of intensive fundamental [12–20] and more application oriented [21–24] research.

At the same time, the main attention is paid to either infinite systems or to structures with simple flat surfaces thus leaving open the question of the effect of restricting geometry. The general objective of the present paper is to address this question by discussing main spectral features of excitations propagating in a WSM wire of finite radius.

One of the difficulties in describing finite WSM structures is to specify correctly the hard boundary conditions, which ensure that the electrons remain inside the material. The problem of boundary conditions imposed on solutions of

the Dirac equation started to attract special attention in the context of states with reduced dimensionality (see Ref. [25] and references therein) almost a half-century ago but still is a subject of research [26–28]. One of the reasons for such delayed development is a drastic difference between the dynamical origins of the hard boundary for the canonical Schrödinger case, which essentially follows prescriptions of the classical mathematical physics, and for a Dirac particle. In the nonrelativistic case, the hard boundary is equivalent to the presence of a sufficiently high potential barrier. Such a barrier supports only attenuated solutions in the prohibited region, which eventually leads to the simple requirement of a vanishing Schrödinger wave function at the boundary. This approach, however, does not work for a Dirac equation due to the Klein tunneling [29–32]. Indeed, the scalar potential raises the level of the Dirac sea and, as a result, a sufficiently high scalar potential barrier instead of blocking propagation opens new propagating channels. Thus, a scalar potential cannot support the hard boundary and a more general class of matrix potentials [33–35] must be considered yielding a manifold of hard boundary conditions.

We show that despite the fact that confining surfaces may be described by various boundary conditions, it is possible to outline general spectral features, which hold at almost all boundary conditions. One of such common features is a series of bands of massive excitations existing at positive and negative energies. The existence of such bands may appear a natural consequence of hard boundary conditions similar to those in classical electrodynamic and quantum Schrödinger systems. It is well known, however, that this picture does not hold of systems governed by the Dirac equation, where, for instance, near hard boundaries may exist surface, or edge, states, which are impossible in the canonical systems. We show that, in WSM wires with the finite radius, such additional states are in general massive due to the boundary induced coupling between states with different helicities. The only class of boundary conditions admitting massless excitations is the one corresponding to fully decoupled helicities and, as a consequence, prescribing the definite orientation of the electron spin at the surface of the wire.

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II. DISPERSION EQUATIONS OF GUIDED MODES

Within the model with two Weyl points, the dynamics of Weyl fermions is described by a Dirac equation with a helicity dependent scalar and vector potentials accounting for separation of the Weyl points:

$$i(\gamma^0 \partial_0 + v \boldsymbol{\gamma} \cdot \nabla) \tilde{\Psi} = \hat{U}(\mathbf{r}) \tilde{\Psi}, \quad (1)$$

where we have introduced the full potential

$$\hat{U}(\mathbf{r}) = eV(\mathbf{r}) + \gamma^5 q_0(\mathbf{r}) + v \boldsymbol{\gamma} \cdot [e\mathbf{A}(\mathbf{r}) + \gamma^5 \mathbf{q}(\mathbf{r})]. \quad (2)$$

Here $V(\mathbf{r})$ and $\mathbf{A}(\mathbf{r})$ are the scalar and vector potential, respectively, and $q_0(\mathbf{r})$ and $\mathbf{q}(\mathbf{r})$ are half-distances between the Weyl points in the energy and in the momentum space.

We employ the fact that both physical potentials and the separations between the Weyl points are spatially uniform inside the wire and thus vector potentials can be excluded with the help of a gauge transformation

$$\tilde{\Psi}(\mathbf{r}) = \exp\{-ie\mathbf{A} \cdot \mathbf{r} - i\gamma^5 \mathbf{q} \cdot \mathbf{r}\} \Psi(\mathbf{r}). \quad (3)$$

Additionally, taking into account that spatially uniform physical potentials lead to simple shifts of the energy and the momentum, we assume that $V = 0$ and $\mathbf{A} = 0$. This turns (1) into an equation with $\hat{U} = 0$ and thus possessing the cylindrical symmetry. Furthermore, we make use of the translational symmetry along the axis of the wire and separate longitudinal and transversal variables. Thus, distinguishing sectors with opposite helicities

$$\Psi(\mathbf{r}) = \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix}, \quad (4)$$

and choosing the z axis along the axis of the wire, we obtain the equations of motion within each sector

$$(\epsilon_\xi + \xi k_\xi \sigma_z) \psi_\xi(\mathbf{r}_\perp) = i \xi \boldsymbol{\sigma}_\perp \cdot \nabla_\perp \psi_\xi(\mathbf{r}_\perp), \quad (5)$$

where $\epsilon_\xi = \epsilon - \xi q_0$, $k_\xi = k + \xi q_z$, $\mathbf{r}_\perp$ is the radius vector in the (x, y) plane, $\boldsymbol{\sigma}_\perp \cdot \nabla_\perp = \sigma_x \partial/\partial x + \sigma_y \partial/\partial y$, and we have chosen units with $v = 1$.

Finally, the rotational symmetry yields the representation

$$\psi_\xi(\mathbf{r}_\perp) = \sum_{m=-\infty}^{\infty} e^{i(m+1/2)\phi} \hat{R}_z(\phi) \psi_\xi^{(j)}(r), \quad (6)$$

where $\hat{R}_z(\phi) = e^{-i\sigma_z \phi/2}$ accounts for rotation of the spin while encircling the origin and $j = m + 1/2$ is the z projection of the total angular momentum.

A general solution of the radial equation corresponding to projection j , up to a normalization factor, can be written as

$$\psi_\xi^{(j)}(r) = \begin{pmatrix} f_\xi^{(1)} J_{j-1/2}(Q_\xi r) \\ i f_\xi^{(2)} J_{j+1/2}(Q_\xi r) \end{pmatrix}, \quad (7)$$

where J_n are the Bessel functions of the first kind, $Q_\xi = \sqrt{\epsilon_\xi^2 - k_\xi^2}$, and we have chosen $f_\xi^{(1,2)} = \xi k_\xi \mp (\xi Q_\xi + \epsilon_\xi)$ in the form emphasizing a symmetry between the components with positive and negative j . In the latter case, one needs to use the relation $J_{-|n|} = (-1)^n J_{|n|}$.

Depending on whether Q_ξ is real ($\epsilon_\xi^2 > k_\xi^2$) or imaginary ($\epsilon_\xi^2 < k_\xi^2$), the state described by Eq. (7) either extends over the whole cross section of the wire or is localized near the

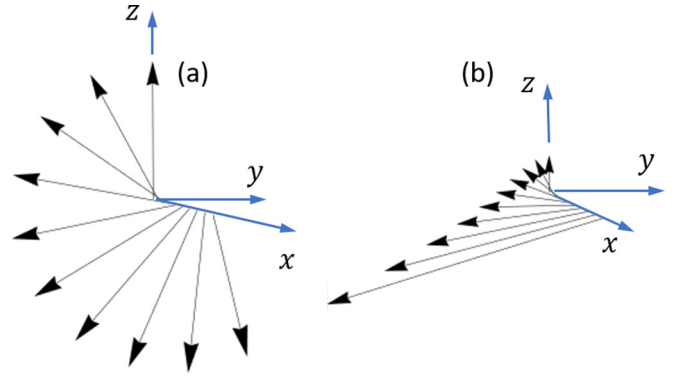


FIG. 1. The variation of the spin in a state propagating in a WSM wire with the axis parallel to the z axis along the radius (the x axis) in (a) extended and (b) surface modes. At the origin, the spin is parallel or antiparallel to the z axis for $j = \pm 1/2$. The spin is confined to the (y, z) plane for all x and experiences full revolutions (for sufficiently large r) for $Q_\xi^2 > 0$ and hyperboliclike rotation for $Q_\xi^2 < 0$.

boundary thus forming surface (edge) states. The case $Q_\xi = 0$ corresponds to an algebraic variation with the distance to the axis of the wire and requires a special consideration (see Appendix A). An important feature of the radial dependence of the spin state must be emphasized: at the axis of the wire, the spin is oriented along or against the axis depending on the sign of the angular momentum and, away from the axis of the wire, the spin lies in the plane normal to the radius (see Fig. 1).

Solutions (7) are subjects to boundary conditions. As has been discussed in the Introduction, there is a manifold of possible boundary conditions corresponding to fermions confined to the interior of the wire. Restrictions imposed on this manifold translate into physical conditions, which, while may take place in particular systems, may be too restrictive to be adopted on the general ground. For example, requiring decoupled character of states with opposite helicities implies a rather special requirement for the spin of Weyl fermions to have definite orientation on the surface of the wire. Indeed, absent radial current $\langle \Psi | \boldsymbol{\alpha} \cdot \mathbf{n}_B | \Psi \rangle|_{r=r_B} = 0$ means that within each helicity sector the spin should be tangent to the surface of the wire and then, due to linearity, all states must have spin with the same orientation.

As we show in Appendix B, a general boundary condition imposed at the surface of the wire can be written as

$$\hat{M} \Psi(r_B) = \Psi(r_B), \quad (8)$$

with the matrix $\hat{M}$ having in the rotated frame $\tilde{M} = e^{i\Sigma_z \phi/2} \hat{M} e^{-i\Sigma_z \phi/2}$, the form

$$\tilde{M} = \hat{M}_\parallel(\mathbf{v}_+, \mathbf{v}_-) \cos \Lambda + \hat{M}_\perp(\theta, \chi) \sin \Lambda, \quad (9)$$

where Λ is the helicity mixing angle, unit vectors $\mathbf{v}_\xi$ lying in the (y, z) plane describe the “pinned” spin states of Weyl fermions with helicity ξ , and the matching angle θ quantifies the rotation around the x -axis aligning vectors $\mathbf{v}_\xi$ so that $\mathbf{v}_+ = -R_x(\theta) \mathbf{v}_-$.

Imposing condition (8) on a solution, one finds a dispersion equation $D(\epsilon, k) = 0$ relating the energy and the longitudinal momentum of the modes propagating along the wire with

$$D(\epsilon, k) = \frac{1}{2} \langle \bar{\psi}_- | R_x^{-1}(\theta) [\sigma_0 - \mathbf{v}_+ \cdot \boldsymbol{\sigma} \cos(\Lambda)] | \psi_+ \rangle, \quad (10)$$

where $\langle \bar{\psi}_- |$ is a state satisfying

$$\langle \bar{\psi}_- | -\mathbf{u} \rangle = -\langle \mathbf{u} | \psi_- \rangle \quad (11)$$

for any unit vector $\mathbf{u}$ in the (y, z) plane, so that for $\psi_- = (\psi_-^{(1)}, \psi_-^{(2)})^T$ one has $\langle \bar{\psi}_- | = i(\psi_-^{(2)}, -\psi_-^{(1)})$.

In the limit $\Lambda = 0$, Eq. (10) yields the dispersion equation for decoupled helicities with the spin states related by $\mathbf{v}_+ = -R_x(\theta)\mathbf{v}_-$, as discussed in Appendix B. In this case, the dispersion equation factorizes $D(\epsilon, k) = D_+(\epsilon, k; \mathbf{v}_+)D_-(\epsilon, k; \mathbf{v}_-)$, where

$$D_{\pm}(\epsilon, k; \mathbf{v}_{\pm}) = \langle -\mathbf{v}_{\pm} | \psi_{\pm} \rangle. \quad (12)$$

In the opposite limit of strong coupling, $\Lambda = \pi/2$, the dispersion equation ensures that the spin states of fermions with different helicities are directly related to each other at the surface of the wire. In this case, one has $D(\epsilon, k) = D(\epsilon, k; \theta)$, with

$$D_{\pm}(\epsilon, k; \theta) = \langle \bar{\psi}_- | R_x^{-1}(\theta) | \psi_{\pm} \rangle. \quad (13)$$

Generally, expanding σ_0 in (10) in terms of eigenstates of $\mathbf{v}_+ \cdot \boldsymbol{\sigma}$, the dispersion equation can be presented in the form explicitly showing the transition between these limiting cases:

$$D(\epsilon, k) = D(\epsilon, k; \theta) \sin^2(\Lambda/2) - D_+(\epsilon, k; \mathbf{v}_+)D_-(\epsilon, k; \mathbf{v}_-) \cos(\Lambda). \quad (14)$$

III. SPECTRA OF PROPAGATING STATES

We limit our analysis of the dispersion relations to the case when the system possesses the full cylindrical symmetry. This takes place when $\mathbf{q}_{\perp} \equiv 0$, so that the Weyl points may only be separated in energy and along the z axis in the momentum space. Even in this case, the spectrum of fermions in WSM wires is very feature rich owing to multidimensionality of the manifold of boundary conditions. We, therefore, limit ourselves to discussing general spectral properties, which hold for a wide variety of boundary conditions, and pay the most attention to an important effect of the restricting geometry of WSM wires: boundary induced mass of excitations.

A. Decoupled helicities

In the case of decoupled helicities, the effect of the separation between the Weyl points reduces to simple shifts of the energy and the longitudinal wave number. Therefore, in order to simplify the notations, we assume that the Weyl points are not separated and omit the helicity index ξ where it is irrelevant.

Making use of the explicit expressions for $\psi_{\xi}^{(j)}$, we obtain

$$D_{\xi}(\epsilon, k; \mathbf{v}_{\xi}) = \sin(\beta_{\xi}/2) f_{\xi}^{(1)} J_{j-1/2}(Qr_B) + \cos(\beta_{\xi}/2) f_{\xi}^{(2)} J_{j+1/2}(Qr_B), \quad (15)$$

where β_{ξ} is the angle between $\mathbf{v}_{\xi}$ and the z axis.

It must be noted that $D_{\xi}(\epsilon, k; \mathbf{v}_{\xi})$ identically vanishes at $\epsilon = \xi k$. This is the consequence of inadequate representation of solutions for the radial equation in form (7) for the case when $Q = 0$. We present a detailed analysis of this case in Appendix A, where we show that modes corresponding to $\epsilon = \xi k$ may exist only for boundary conditions of the special form $\mathbf{v}_{\xi} = -\xi \mathbf{e}_z$. In what follows, we assume that this

condition is not met and, therefore, solutions of $D_{\xi}(\epsilon, k; \mathbf{v}_{\xi}) = 0$ corresponding to $\epsilon = \xi k$ must be excluded.

The gapped solutions of $D_{\xi}(\epsilon, k; \mathbf{v}_{\xi}) = 0$ correspond to standing cylindrical waves inside the wire and thus emerge at energies yielding relatively large values of arguments of the Bessel functions in (15). Taking this into account, we obtain in the limit of small k the dispersion laws of the massive states for $\epsilon > 0$ and $j = 1/2$ in the form

$$\epsilon_{\xi}^{(l)}(k) = \mu_{\xi}^{(l)} + \frac{k^2}{2\mu_{\xi}^{(l)}}, \quad (16)$$

where integer l enumerates subbands, and the masses of the excitations are

$$\mu_{\xi}^{(l)} = \frac{1}{2r_B} \left(\beta_{\xi} + \frac{\pi}{2} + 2\pi l \right). \quad (17)$$

For negative energies, the subbands have negative masses $\epsilon_{\xi}^{(l)}(k) = -\mu_{\xi}^{(l)} - \frac{k^2}{2\mu_{\xi}^{(l)}}$ with $\mu_{\xi}^{(l)} = (\beta_{\xi} + 2\pi l - \pi/2)/2r_B$.

The presence of massive excitations may appear a natural consequence of the hard boundary conditions (cf. a Schrödinger particle in a confining potential or the electromagnetic field in a conducting hollow waveguide). It is important, therefore, to emphasize that, despite strong confinement, in addition to massive states there are also massless excitations. In order to qualitatively describe them, we consider the solutions of $D_{\xi}(\epsilon, k; \mathbf{v}_{\xi}) = 0$ near the point where they cross the $Q = 0$ states with a nontrivial spin orientation (see Appendix A). Employing the smallness of Q , we can approximate Eq. (7) by

$$\psi_{\xi}^{(j)} \propto \begin{pmatrix} -1 \\ (\xi\epsilon_{\xi} + k_{\xi}) \frac{i}{K^{(j)}} \end{pmatrix}, \quad (18)$$

where

$$K^{(j)} = \frac{2j+1}{r_B} \quad (19)$$

defines a characteristic spatial and energy scale induced by the finite radius of the wire.

Using Eq. (18), we find the spectrum of massless excitations for positive projections of the total angular momentum

$$\epsilon_{\xi}^{(j)}(k) = K^{(j)}(\beta_{\xi}) - \xi k, \quad (20)$$

where $K^{(j)}(\beta_{\xi}) = K^{(j)} \tan(\beta_{\xi}/2)$.

For $j < 0$, we have $\epsilon_{\xi}^{(j)}(k) = -[\bar{K}^{(j)}(\beta_{\xi}) - \xi k]$, with $\bar{K}^{(j)}(\beta_{\xi}) = (2|j|+1)r_B^{-1} \cot(\beta_{\xi}/2)$.

Figure 2 presents the results of the numerical solution of $D_+(\epsilon, k; \mathbf{v}_+) = 0$ together with the results obtained from (20) for different orientations of the pinned spin state. It shows that for small β_{ξ} , when $K^{(j)}(\beta_{\xi})r_B$ is small, approximation (18) reproduces main spectral features satisfactorily.

The massless states change their character from extending over the cross section of the wire [for $|k| < K^{(j)}(\beta_{\xi})/2$] to surface modes [when $|k| > K^{(j)}(\beta_{\xi})/2$]. Thus, in this case, the dispersion curves of the surface states are rays with the termination points $k_c = K^{(j)}(\beta_{\xi})/2$ except for $\beta_{\xi} = 0$, when the whole spectral branch corresponds to the spin distribution algebraically decaying with the distance from the surface of the wire.

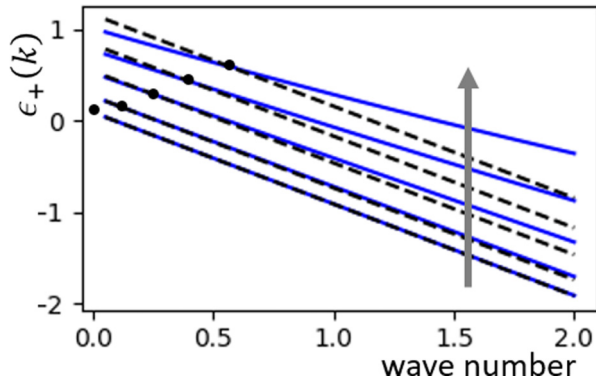


FIG. 2. The dispersion laws $\epsilon_+(k)$ of the gapless modes obtained numerically (solid lines) and from (20) (dashed lines) for different angles between the pinned spin state and the z axis, $\beta_+ = 5^\circ, 15^\circ, 30^\circ, 45^\circ, 60^\circ$. The arrow shows the variation of the lines with increasing β_+ . The dots indicate the transition from the state extending over the cross section of the wire [$k < K^{(j)}(\beta_+)/2$] to surface states [$k > K^{(j)}(\beta_+)/2$].

B. Strong coupling between helicities

A similar analysis as in the previous section can be used for discussion of some general spectral features in the case of strong coupling $\Lambda = \pi/2$. Indeed, Eq. (13) can be interpreted as if the pinned state at the surface of the wire is given by the spin state of the fermions with the complementary helicity. Since the general form of the features discussed above does not depend on the precise orientation of the boundary spin, they preserve in the limit of strong coupling as well.

The main changes induced by the strong coupling happen at a vicinity of anticrossing of dispersion curves corresponding to decoupled helicities. Near these points, we can use an approximation similar to (18) for both $|\psi_+\rangle$ and $\langle\bar{\psi}_-|$. Expanding the resultant equation, one can see that it contains the energy, the longitudinal momentum, and the separation between the Weyl points only in combinations

$$\bar{\epsilon} = \epsilon + q_z, \quad \bar{k} = k - q_0. \quad (21)$$

Thus, the spectrum of systems with different separations will have the same form as discussed below up to shifts in the (ϵ, k) plane. It should be noted in this regard that the separation of the Weyl points in energy q_0 induces shifts along the k axis, while q_z results in shifts along the energy axis.

Solving the resultant quadratic equation with respect to $\bar{\epsilon}$, we find

$$\bar{\epsilon}_{u,b}(\bar{k}) = \Delta(\pi/2) \cos(\theta/2) \pm \sqrt{\bar{k}^2 + \Delta^2(\pi/2)}, \quad (22)$$

where

$$\Delta(\pi/2) = \frac{K}{\sin(\theta/2)} \quad (23)$$

is the mass of the low-energy excitations acquired due to the boundary induced coupling between helicities. Figure 3 presenting a comparison of these results with numerical solutions of $D(\epsilon, k; \theta) = 0$ shows that the adopted approximation reproduces very well the spectrum of excitations near the extrema of the bands.

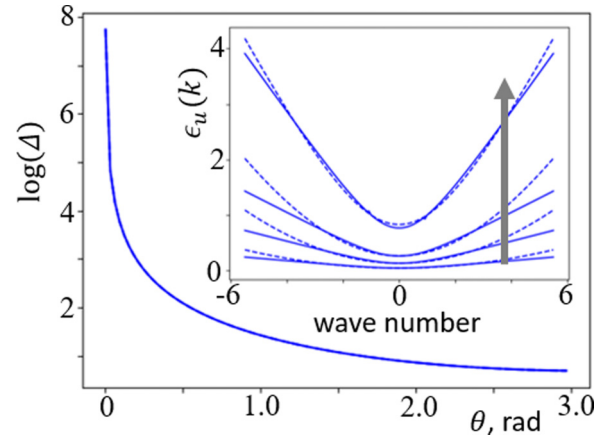


FIG. 3. Natural logarithm of the half-width of the gap (or the mass) induced by the boundary condition corresponding to a strong coupling as a function of the matching angle θ . The numerical and analytical results are indistinguishable on this scale. The inset shows the upper branch of the massive excitations, found by numerical solution of $D(\epsilon, k; \theta) = 0$ (solid lines) and from (22) (dashed lines) for different values of the matching angle $\theta = 5^\circ, 15^\circ, 30^\circ, 90^\circ$ (the arrow shows the variation of the branch with increasing θ).

It must be emphasized that the acquired mass is the consequence of restricted geometry in the radial direction. With increasing the radius of the wire, the mass decreases and vanishes in the limit $R \rightarrow \infty$ corresponding to the well studied case of a WSM with a flat surface. At the same time, as follows from Eq. (23), the acquired mass is not bounded from above and diverges as θ approaches 0. In this limit, the spectrum consists of a single flat band at $\bar{\epsilon} = 0$, while the second band escapes to infinity. The emergence of the flat band can be seen in the case $q_z = q_0 = 0$ directly from Eq. (13). Indeed, for $\theta = 0$, we have

$$D(\epsilon, k; \theta = 0) = 2\epsilon k J_m(Qr) J_{m+1}(Qr), \quad (24)$$

which vanishes either at isolated points or when $\epsilon(k) \equiv 0$.

Finally, it should be noted that changing the sign of the gap when θ passes through zero corresponds to changing the character of the low energy band. It reaches minimum or maximum at $\bar{k} = 0$ and shifts upwards or downwards with increasing magnitude of θ for positive and negative θ , respectively.

C. General boundary conditions

In view of Eq. (14), traversing the manifold of boundary conditions should yield a continuous transition to the strong coupling limit. As a result, the main spectral features found for the case $\Lambda = \pi/2$, in particular, opened gap in the spectrum of excitations massless when the helicities are fully decoupled, should preserve for the general case as well.

Using the same approach as in the previous section, we obtain an equation with respect to $\bar{\epsilon}$ with the solutions

$$\bar{\epsilon}_{u,b}(\bar{k}) = \Delta(\Lambda) \frac{\sin(\delta)}{\sin \Lambda} \pm \sqrt{[\bar{k} - k_D(\Lambda)]^2 + \Delta^2(\Lambda)}, \quad (25)$$

where we have excluded θ using the relation $\beta_+ - \beta_- = \theta + \pi$ and denoting $\delta = (\beta_+ - \beta_-)/2$. The mass of low-energy

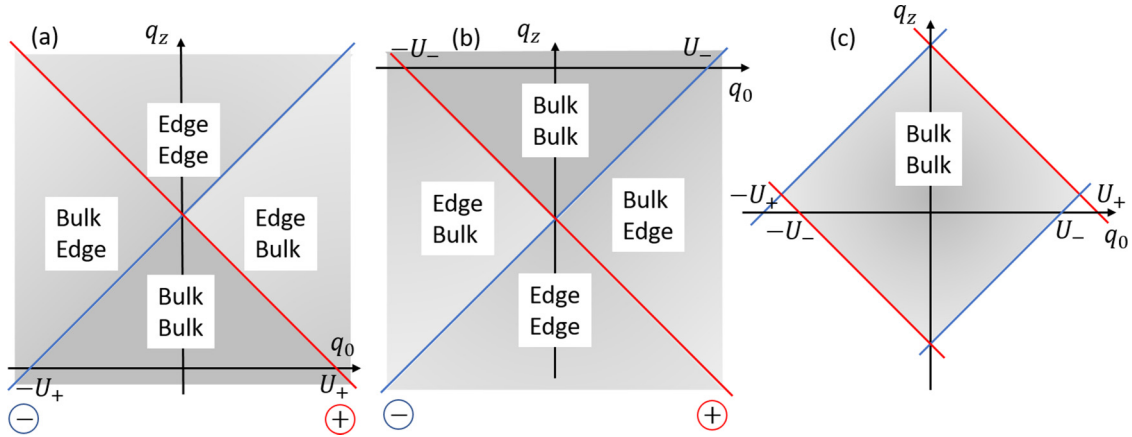


FIG. 4. The phase diagram on the (q_0, q_z) plane of the structure of states occupying the upper (a) and the lower (b) branches (for $\theta > 0$) of the excitations gapped due to coupling between states with opposite helicities at the surface of the WSM wire. The transition lines corresponding to different helicities are identified by encircled + and -. In specifications of the structure of the state (bulk or edge), the upper and lower lines are for $\xi = 1$ and $\xi = -1$, respectively. (c) Diagrams for different branches superimposed to indicate the region where all states have the same structure.

excitations is

$$\Delta(\Lambda) = K \frac{\sin(\Lambda)}{\cos(\Lambda) \cos(\bar{\beta}) + \cos(\delta)}, \quad (26)$$

with $\bar{\beta} = (\beta_+ + \beta_-)/2$, and the position of the extrema of the bands is given by

$$k_D(\Lambda) = \Delta(\Lambda) \cot(\Lambda) \sin(\bar{\beta}). \quad (27)$$

Equation (26) defines a subset of boundary conditions producing the flat band in the spectrum of WSM wires

$$\cos(\Lambda) \cos(\bar{\beta}) + \cos(\delta) = 0. \quad (28)$$

Using the obtained results, one can show that states near the edges of the opened gap can be either bulk or surface depending on separation between the Weyl points. The character of the spatial variation of the state in the radial direction is determined by the sign of $Q_\xi^2 = \epsilon_\xi^2 - k_\xi^2$. Substituting the solution obtained above, we obtain that the vicinity of the minimum of the upper (for $\delta > 0$) branch is occupied by bulk modes, if

$$U_+ - (q_z + \xi q_0) > 0. \quad (29)$$

In turn, the top of the lower branch corresponds to bulk modes, if

$$U_- + (q_z + \xi q_0) > 0, \quad (30)$$

where

$$U_\pm = \Delta(\Lambda) \left[\frac{\sin(\delta)}{\sin(\Lambda)} \pm 1 \right]. \quad (31)$$

We present these results in Fig. 4 in the form of a phase diagram on the (q_0, q_z) plane of separations between the Weyl points. The straight lines separate the regions where the extrema of the separated bands correspond to bulk and surface modes and are determined by the boundary conditions only. In Fig. 4(c) we superimpose diagrams for the lower and upper bands to emphasize that for small separations $q_{0,z}$ the near-edge (nonrelativistic) states are bulk modes. At the same time it should be noted that with increasing the radius of the wire,

the middle region in Fig. 4(c) shrinks relaxing the condition imposed on the separation of the Weyl points.

IV. CONCLUSION

We have studied the effect of restricting geometry on the spectrum of excitations in Weyl semimetals (WSMs) using as a model a cylindrical WSM wire.

We have parametrized the full manifold of hard boundary conditions imposed by the requirement of vanishing amplitude of finding an electron outside of the wire. The most general boundary conditions are described by two distributions of unit vectors tangent to the surface of the wire, and the distributions of a scalar coupling parameter and a relative phase between the states with different helicities.

We derive the general form of the dispersion equation relating energy and longitudinal momentum of electrons propagating along the wire. The coupling parameter describes a continuous transition between the limit of decoupled helicities when the boundary conditions have the form of pinned spin states at the surface of the wire, to the strong coupling case, where the rotational symmetry is restored at the surface but by the price of a direct relation between the orientations of the spins of electrons with different helicities.

We study main spectral features following from the derived dispersion equation. We show that in the limit of decoupled helicities, for each helicity, the spectrum consists of massive bands and a single massless band. At the same time, we show that the presence of massless bands is specific for systems with the boundary conditions supporting decoupled helicities. Since relaxing the spin state at the surface of the wire is achieved by coupling states with different helicities, this leads to lifting the degeneracy at the point of anticrossing resonance with opening a gap in the spectrum and, thus, creating two massive modes. The acquired mass is a result of the confined geometry in the radial direction and vanishes in the limit of infinite radius of the wire (flat surface).

This demonstrates that restricting geometry may lead to strong modifications of the spectral properties of WSMs and may lead to formation of new classes of excitations.

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APPENDIX A: ZERO-MASS MODES

A straightforward substitution of $\epsilon_\xi = \xi k_\xi$ into (7) yields a trivial solution $\psi_\xi^{(j)}(r) \equiv 0$. Here we derive a correct form of solutions of

$$(\epsilon + \xi k \sigma_z) \psi(\mathbf{r}_\perp) = i \xi \sigma_\perp \cdot \nabla_\perp \psi(\mathbf{r}_\perp), \quad (\text{A1})$$

for $Q_\xi \equiv \sqrt{\epsilon^2 - k^2} = 0$. Here and below, we assume that both external potentials and separations between the Weyl points are absent, since they only lead to, generally speaking helicity dependent, shifts of the energy, and longitudinal momentum.

We notice that $Q_\xi = 0$ corresponds to the case when $\epsilon + \xi k \sigma_z$ has a zero eigenvalue. This simplifies (A1) to a system of equations, which can be directly integrated using, for example, the characteristics method. This presents the solution in terms of analytical functions of $\tau_\pm = e^{\pm i \phi} r$. Among the full set of solutions, we are the most interested in those induced by the series representation of the analytical functions, which establishes a connection with representation in terms of states with the definite projection of the angular momentum on the z axis. Thus, taking into account the condition of regularity at the origin, it is convenient to introduce

$$h_s^{(m)} = (e^{i s \phi} r)^m, \quad (\text{A2})$$

and to approach Eq. (A1) directly having in mind the relations

$$(\partial/\partial x \pm i \partial/\partial y) h_s^{(m)} = m(1 \mp s) h_s^{(m-1)}. \quad (\text{A3})$$

This leads to a solution of Eq. (A1) in the form (up to a normalization factor)

$$\psi(r, \phi) = \begin{pmatrix} a h_s^{(n)} \\ b h_s^{(m)} \end{pmatrix}. \quad (\text{A4})$$

One class of solutions corresponds to either a or b equal to zero, so that the spin is parallel to the z axis. The spectrum of these excitations consists of two branches $\epsilon = \pm k$, with $\psi_\xi^{(m)} = h_{-\xi}^{(m)} |-\xi z\rangle$ on $\epsilon = k$, and $\psi_\xi^{(m)} = h_\xi^{(m)} |\xi z\rangle$ on $\epsilon = -k$.

Additionally, we find that for $s > 0$ there are solutions existing when $\epsilon = \xi k$ and $n = m - 1$ with $a = im$ and $b = k$. For $s < 0$, the nontrivial solutions exist when $\epsilon = -\xi k$ and $n = m + 1$ with $a = -k$ and $b = in$.

It should be emphasized that for both these classes of solutions, Weyl fermions with opposite helicities occupy the same spectral branch with opposite projections of the total angular momentum. This is, essentially, a consequence of the requirement of regularity at the origin. It should be noted in this regard, that in hollow wires, the power of monomials is no longer limited by non-negative values. This lifts restrictions on the sign of the angular momentum (cf. modes of the electromagnetic field guided by hollow cables [36]).

APPENDIX B: PARAMETRIZATION OF THE FAMILY OF LOCAL BOUNDARY CONDITIONS

At the boundary of the wire, the wave function must satisfy a boundary condition $\Psi = \hat{M} \Psi$ with such Hermitian $\hat{M}$ that ensures vanishing current through the surface of the wire $j_n = \langle \Psi | \mathbf{n}_B \cdot \boldsymbol{\alpha} | \Psi \rangle = 0$, with $\mathbf{n}_B$ being the normal to the surface. Such boundary conditions in the context of the Dirac equation have been discussed in a number of publications (see, e.g., [33–35]). We, however, need $\hat{M}$ represented in a way emphasizing coupling between particles with different helicities, which is slightly different from previously used representations.

The matrix $\hat{M}$ must satisfy the anticommutation relation $\{\hat{M}, \mathbf{n}_B \cdot \boldsymbol{\alpha}\} = 0$ and can be chosen unitary, so that $\hat{M}^2 = \hat{1}$. In the cylindrical coordinate system, in the rotated spinor frame with $\Psi = \exp(-i \Sigma_z \phi/2) \tilde{\Psi}$, the radial component of $\boldsymbol{\alpha}$ turns into α_x and for $\tilde{M} = e^{i \Sigma_z \phi/2} \hat{M} e^{-i \Sigma_z \phi/2}$ we have

$$\{\tilde{M}, \alpha_x\} = 0. \quad (\text{B1})$$

The matrix $\tilde{M}$ can be presented in the block form $\tilde{M} = \begin{pmatrix} M_{11} & M_{12} \\ M_{12}^\dagger & M_{22} \end{pmatrix}$, where M_{ij} are 2×2 matrices, which in the chiral representation satisfy $\{M_{ij}, \sigma_x\} = 0$ and $[M_{12}, \sigma_x] = 0$. Thus, for an arbitrary matrix $\tilde{M}$ anticommuting with α_x , we have $M_{ii} = \mathbf{m}_{ii} \cdot \boldsymbol{\sigma}$, $M_{12} = m_{12}^{(0)} \sigma_0 + m_{12}^{(x)} \sigma_x$, where σ_0 is a 2×2 identity matrix, vectors $\mathbf{m}_{ii}$ are tangent to the surface of the wire, and $m_{12}^{(0,x)}$ are arbitrary complex numbers.

Imposing the condition $\tilde{M}^2 = \hat{1}$, we find that the parameters defined above are subjects of several constraints. For example, from equality of the diagonal blocks of $\tilde{M}^2$ to σ_0 , it follows that $m_{ii}^2 + |m_{12}^{(0)}|^2 + |m_{12}^{(x)}|^2 = 1$ and $\text{Re}[m_{12}^{(0)} m_{12}^{(x)*}] = 0$. They show that M_{12} is proportional to a unitary matrix and thus the condition $M_{11} M_{12} + M_{12} M_{22} = 0$ can be regarded as a relation between vectors $\mathbf{m}_{ii}$ and a condition imposed on M_{12} : it must leave vectors $\mathbf{m}_{ii}$ in the tangent plane. Making use of these observations, we can represent

$$\tilde{M} = \hat{M}_\parallel(\mathbf{v}_+, \mathbf{v}_-) \cos \Lambda + \hat{M}_\perp(\theta, \chi) \sin \Lambda, \quad (\text{B2})$$

where Λ is the helicity mixing angle, and

$$\hat{M}_\parallel(\mathbf{v}_+, \mathbf{v}_-) = \begin{pmatrix} \mathbf{v}_+ \cdot \boldsymbol{\sigma} & 0 \\ 0 & \mathbf{v}_- \cdot \boldsymbol{\sigma} \end{pmatrix},$$

$$\hat{M}_\perp(\theta, \chi) = \begin{pmatrix} 0 & e^{i\chi} R_x(\theta) \\ e^{-i\chi} R_x^{-1}(\theta) & 0 \end{pmatrix}. \quad (\text{B3})$$

Here $R_x(\theta) = e^{-i \sigma_x \theta/2}$ is the rotation around the x axis in the spin $1/2$ representation. Vectors $\mathbf{v}_\pm$ are unit vectors in the plane tangent to the surface of the wire and are related by $\mathbf{v}_+ = -R_x(\theta) \mathbf{v}_-$, which can be regarded as either a relation between $\mathbf{v}_\pm$ or a definition of θ .

We consider two important particular cases: $\Lambda = 0$ and $\Lambda = \pi/2$.

In the case $\Lambda = 0$, the states with opposite helicities are decoupled and satisfy their own boundary conditions: $\psi_\xi = \mathbf{v}_\xi \cdot \boldsymbol{\sigma} \psi_\xi$. They correspond to fermion's spins taking definite directions determined by vectors $\mathbf{v}_{1,2}$, in other words the spins are pinned at the surface of the wire.

The second case, $\Lambda = \pi/2$, corresponds to strong coupling. An example of physical situation where such a model appears

naturally is the case when the electron is described by the Dirac equation with zero mass inside the wire and large mass outside. Similar models were widely applied for describing hard boundaries in reduced dimensionalities [37,38]. In this case, physical states are attenuated in the prohibited region due to the mass barrier and the boundary conditions are formulated as orthogonality to unphysical exponentially growing solutions. Solving the Dirac equation and taking the limit of infinite mass outside yields the boundary condition with $\tilde{M} = \hat{M}_\perp$

($\theta = \pi, \chi = -\pi/2$). It should be noted, however, that the spin states inside the material should not necessarily correspond to the spin states in the prohibited region and, thus, a unitary transformation of spin states should be allowed at the boundary yielding the class of boundary conditions with arbitrary θ . The important feature of this model is that it demonstrates that the boundary conditions can be determined by the environment only regardless of dynamical properties inside the wire, in particular, of the separation between the Weyl points.

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