Topological bands in monolayer \( \text{PdSe}_2 \)

Sergio Bravo$^*$ and M. Pacheco

Departamento de Física, Universidad Técnica Federico Santa María, Valparaíso, Chile

J.D. Correa

Facultad de Ciencias Básicas, Universidad de Medellín, Medellín, Colombia

Leonor Chico

Departamento de Física de Materiales, Facultad de Ciencias Físicas, Universidad Complutense de Madrid, 28040 Madrid, Spain

(Dated: February 9, 2022)

The electronic structure of palladium diselenide \( \text{PdSe}_2 \) in its monolayer form is analyzed from the topological band theory perspective. Employing first-principles calculations, effective models and symmetry indicators we found that the low-lying conduction bands are topologically nontrivial, protected by time reversal and crystalline symmetries. Numerical evidence supporting the nontrivial character of the bands is presented and examples of physical responses are discussed.

Two dimensional materials are among the most promising types of systems in the continuous search for novel structures that can give shape to the future technological advances. The low dimensional character of these structures make them ideal candidates for their application in nanoscale devices [1]. Starting with graphene more than a decade ago a vast amount of these layered systems has been proposed [2–4]. Within this emerging group of novel materials, the recently synthesized \( \text{PdSe}_2 \) system has been the subject of intensive experimental and theoretical research. Different forms of the material with a variable number of layers has been reported, possessing high air stability [5–9], which is a remarkable property for their extended (long-term) use. Also, good electrical transport [10], optical [11–14] and thermoelectric properties [15] have been experimentally reported.

On the theoretical side, several works have analyzed the physical properties of the material in its monolayer and multilayer form [16–20]. Among these theoretical accounts the band connectivity and the symmetry-related properties of the electronic structure has not been studied in detail for monolayer \( \text{PdSe}_2 \); we address this issue in this work. Using the theory of symmetry indicators along with first-principles calculations we identify that the lowest conduction bands of monolayer \( \text{PdSe}_2 \) realize a topologically nontrivial phase. These bands comprise a strong topological phase with a well defined topological invariant and gapless edges states that we characterize using well-known numerical methods. Also, a digression about the accessibility of these nontrivial conduction states by Fermi level manipulation is developed. These results open the possibility for the exploration of this promising material and its related structures from the topological point of view.

The article is organized as follows. First an overview of the numerical calculations and parameters used is sketched. Then we present the geometric information and first-principles electronic band structure of monolayer \( \text{PdSe}_2 \) along with a study of the symmetry character of the bands. Additionally, effective models based on Wannier interpolation are briefly described and put forward to study the edge states and the Wannier charge center (WCC) evolution along different directions. As signatures of the nontrivial band character of the material, the shift current and the spin Hall conductivity are computed as a function of frequency and chemical potential. Finally, we conclude with a summary and outlook for possible future work. Part of our results are left as Supplementary Information (SI).

Computational details - The calculations for the band structure were carried with standard density functional theory (DFT) methods using the QUANTUM ESPRESSO package [21] at the GGA-PBE level. The monolayer structure was relaxed with a force tolerance of \( 10^{-4} \) eV/Å. The energy cutoff for the plane wave basis was 100 Ry with a vacuum distance of 20 Å in the perpendicular direction to the monolayer. A Monkhorst-Pack grid of \( 15 \times 15 \times 1 \) was chosen and the energy convergence tolerance was set to \( 10^{-8} \) Ry. The Wannier interpolation of the DFT energy bands was performed with the Wannier90 code [22]. Two models were implemented: a twelve-band (12B) model including the four uppermost valence bands and the eight lowest conduction bands and a eight-band (8B) model that only includes the above mentioned conduction bands. This second model was used to focus only on the nontrivial bands of the system. For the 12B model, \( d \)-orbitals were used for the Pd atoms and \( p \)-orbitals for the Se atoms. These orbitals were only used as starting sites for the orbitals as the location of the Wannier centers may change under the wannierization process. The post-processing of Wannier-based models was carried by the PythTB code [23]. Also, Wannier90 was used to analyze this model and to calculate the optical responses presented below. The mathematical expressions implemented in this code are based on [24, 25] and for quick reference they are also

$^*$ sergio.bravo.14@sansano.usm.cl
Lattice geometry and space group - The lattice structure of PdSe$_2$ is composed of irregular (type 4) pentagons forming a buckled geometry as presented in Fig.1 a). Pd atoms are four-fold coordinated and Se atoms have coordination three. As previous works reported [5], the crystalline order conforms a tetragonal lattice, with three symmetry operations; a two-fold rotation around one of the lattice vectors axis with fractional translation (1/2,1/2,0) in terms of the unit cell vectors, a mirror glide plane and spatial inversion [26]. This has to be complemented with time reversal (TR) symmetry to give the space group (SG) P2$_1$c or SG #14. Within this frame the Pd atoms sit at the 2$a$ Wickoff position (WP) while the Se atoms locate at the 4$e$ WP [26]. The relaxed structure obtained from our first-principles calculations comprises a rectangular unit cell with lattice vectors with magnitude $a$ = 5.74 Å and $b$ = 5.91 Å. The calculation also yields a monolayer thickness of 0.7 Å, confirming the buckled geometry of the material. These results agree well with the reported experimental and theoretical values [5, 16, 20].

Electronic band structure and symmetry indicators - The band structure of monolayer PdSe$_2$ has been extensively studied in previous works [5, 16–20]. Here we focus on the band connectivity an associated topological properties of the low energy bands around the Fermi level. For this purpose we present in Fig.1 c) the electronic band structure including spin-orbit coupling (SOC) at the PBE level along the high-symmetry path $\Gamma-Z-D-B-\Gamma$ in momentum space (Brillouin zone is depicted in Fig. 1 b), following the notation of [27]). The SOC addition is crucial for the results obtained as will be clarified in what follows. As it is well-known, PBE results systematically underestimate the fundamental gap in semiconductors and insulators, thus we have checked for other works that compute the electronic structure of monolayer PdSe$_2$ with Hybrid (HSE06) functional [17] and at the GW level [28]. These more expensive calculations show a larger band gap but keep the band general features unaltered, giving validity for the topological analysis using the PBE functional. From the band structure and the space group information it can be confirmed that all bands are doubly degenerated along the whole Brillouin zone (BZ) as monolayer PdSe$_2$ is centrosymmetric (SG#14). The inclusion of SOC - associated to the use of double space groups - affects the degeneracies of the system with no SOC, leaving the possibility of only four-fold nodal points at the Z and D points. These points are protected by the nonsymmorphic symmetries of the SG in conjunction with time-reversal symmetry [29]. These four-fold nodal points are present in every group of four bands in the structure. This is the basic ingredient for the band connectivity of the system, since as prescribed by the topological quantum chemistry theory [30], these sets of four bands form what is known as a band representation [31]. To start the study of the topological properties of monolayer PdSe$_2$ the first step is to search for a signature of nontrivial topology in the SG #14. The most natural attempt is to look for strong topology as this is the most widely known type of nontrivial phase. In order to check this we use the results of Ref.[32], adapted for the case of a two dimensional BZ. In [32] a Smith normal form decomposition is applied to the set of elementary band representations (EBR) of the SG. EBR are the building blocks to construct the bands of atomic insulators and as such, can be mapped directly to exponentially localized Wannier functions [33] situated at the atomic positions of the material. Using these EBR the procedure is briefly sketched as follows. First an EBR matrix is constructed, including as coefficients the multiplicities of the irreducible representations (IR) at the high-symmetry points of the material (Γ,Z,D,B for our particular case). The elements of the EBR matrix are provided in Table I (using the Bilbao Crystallographic Server information [27]). Next the smith normal form matrix $\Delta$ is calculated, which is a diagonal matrix with positive integer values. If some of these values is greater than one, then a strong topological phase is possible for the SG [32]. The $\Delta$ matrix for the (2D) SG#14 is given by.

$$\Delta = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

We observe that a diagonal element with value 2 is present, which allows for a $Z_2$ phase in the system [32]. Thus, strong topological bands are in principle possible in this SG. This phase is a version of the time reversal plus inversion topological phase [34], which in this case is further enriched by the other crystalline symmetries of the group. The presence of these additional symmetries simplifies the symmetry indicated character of the nontrivial topology. This can be seen in the definition of the above mentioned $Z_2$ invariant. Further manipulation of the EBR matrix (see the SI for this particular group or [32] for the general theory) gives as a result that the $Z_2$

| IR/EBR | EBR1 | EBR2 | EBR3 | EBR4 |
|--------|------|------|------|------|
| Γ$_3$Γ$_4$ | 2 | 2 | 0 | 0 |
| Γ$_5$Γ$_6$ | 0 | 0 | 2 | 2 |
| D$_3$ | 1 | 0 | 1 | 0 |
| D$_4$ | 1 | 0 | 1 | 0 |
| D$_5$ | 0 | 1 | 0 | 1 |
| D$_6$ | 0 | 1 | 0 | 1 |
| Z$_2$ | 1 | 1 | 1 | 1 |
| B$_2$ | 1 | 1 | 1 | 1 |

TABLE I. Elements of the EBR matrix for the two dimensional SG#14.
invariant only depends on the parity of the $\Gamma$ point IR. In this double SG $\Gamma$ have only two IR: $\Gamma_3\Gamma_4$ and $\Gamma_5\Gamma_6$ \cite{35}. With this definition the topological invariant for the strong phase can be defined as

$$Z_2 = n_{\Gamma_3\Gamma_4} \pmod{2} = n_{\Gamma_5\Gamma_6} \pmod{2},$$ \hfill (2)

where $n_{\Gamma_3\Gamma_4}, n_{\Gamma_5\Gamma_6}$ correspond to the multiplicities of the IR at $\Gamma$. In other words, if a single (fourfold) band representation or a group of band representations has an odd number of $\Gamma_3\Gamma_4/\Gamma_5\Gamma_6$ IR, then these bands are topological. This definition of $Z_2$ is simpler than the standard Fu-Kane formula for TR inversion-symmetric insulators \cite{36} due to the further constraints of the above mentioned symmetries. One additional point to mention is that this is the only kind of symmetry-induced topology that can be present in this two-dimensional (layer) version of SG#14. The linear combination of strong band representations gives another strong band representation or yields a trivial band representation. This differs from the three-dimensional version of this group where fragile bands and strong bands can coexist \cite{32}. For monolayer PdSe$_2$ we have computed the IR characters numerically from the first-principles electronic structure using the Ir-Rep package \cite{37}. We studied two groups of bands: the valence band manifold of the material and the eight lowest conduction bands. In the valence bands set there exist an even number of $\Gamma_3\Gamma_4/\Gamma_5\Gamma_6$ IR, which render the material a trivial insulator. On the other hand, if we consider the aforementioned conduction bands, we find that both (fourfold) band representations have separately an odd number of $\Gamma_3\Gamma_4/\Gamma_5\Gamma_6$ IR. Therefore each single group realize a strong topological group of bands. In Fig.1 c) we have labelled the bands with the corresponding IR for the highest valence band representation and for the lowest conduction bands. A crucial role here is played by SOC which permits for band inversion between the two group of band representations. The inversion can be initially identified from the band structure in Fig.1 c), specially along the $B - \Gamma$ line. Further confirmation of the band inversion is presented in Fig.2 a), where the orbital-projected bands are presented. The $p$-orbitals make the most important contribution to the inversion and the effective models for these bands are based on this result.

Evidence of the nontrivial topology - A clearer picture of the nontrivial topology of monolayer PdSe$_2$ can be obtained by the computation of the standard quantities that pinpoint the nontrivial character of the bands. Thus, we calculated the energy dispersion for a ribbon geometry of the material and the bulk Wannier charge center (WCC) evolution along the BZ \cite{38}, using a Wannier-based model. Before delving into these results, we comment on the Wannier centers in real space associated with the conduction bands. We employed a reduced 8B model, as described above, to only account for these bands. These bands are well separated from higher conduction bands, which make them suitable for faithful wannierization. The localization of the Wannier centers in real space for PdSe$_2$ is represented in Fig.2 b). A pair of Wannier centers sits on each site, as dictated by time reversal symmetry (Kramers pairs)\cite{39}. Most importantly, it can be observed that two pairs of these Wannier centers are localized at a WP (2b) that is not occupied by any of the atoms in the material. This obstruction hints for a nontrivial topology \cite{39} and PdSe$_2$ can be dubbed as a conduction band obstructed atomic insulator. The other Wannier centers localize on the 2a WP and thus coincide with atomic (Pd) orbitals. The WCC evolution along the $k_x$ direction in the BZ is presented in Fig3 a). Here we also use the 8B model in order to isolated the nontrivial behavior. For this model we assume that the four lowest conduction bands are occupied, just for the sake to conform with the usual WCC definition \cite{33}. The general trend of the WCC evolution shows the typical features of a TR inversion symmetric topological insulator \cite{34}, with the nontrivial crossings at one of the time reversal invariant momenta (in this case $k_x = \pi$). The energy dispersion of the edge states for a confined geometry is plotted in Fig3 b). In this case we make use of the 12B model, with the aim to show also the fundamen-
nal gap and their edge states. Gapless energy states arise within the gap at \( \approx 0.8 \) eV above Fermi level, localized on the edges of the finite slab, giving further confirmation for the nontrivial phase of the conduction bands. The edge termination has influence on the form of the edges states dispersion but there always exists gapless states in this upper gap. The fundamental gap also presents edges states that are trivial in terms of the above classification. Further information for other edges is presented in the SI.

**Examples of physical response** - The main drawback of the topological bands spotted in the above discussion is that they are situated in the conduction bands, which implies that some external manipulation of the material is necessary in order to access them. This hinder the use of monolayer PdSe\(_2\) as a spin Hall insulator, since the nontrivial gap is not the fundamental gap. Notwithstanding, the lowest conduction bands of the material are reachable by the standard methods of doping and gating \([1, 40]\). As these methods can displace the chemical potential \( \mu \) to lie inside the conduction bands, it is in principle possible to accede the nontrivial bands and to explore the nontrivial behaviour of the material. We simulate this (electron) doping effect by a rigid shift of the chemical potential using the 12B model and calculate two optical responses for different values of \( \mu \) in the conduction band. For the first response we compute the interband contribution to the shift current \( \sigma_{abc} \) for a photon energy up to 2.5 eV, where our low energy model is valid. First-principles calculations of the shift current for non-doped multilayer PdSe\(_2\) have been performed recently giving high output values \([14]\). It is well documented that this shift current is enhanced in presence of topological bands \([41–43]\). We analyze the effect of the chemical potential position of this shift current and present the results in Fig.4 a) for \( \sigma_{yy} \). The slab geometry has been taken into account by a global scaling factor following \([24]\). As expected, the low frequency region is the most directly affected. We have calculated cases with the chemical potential within the conduction band and also inside the (trivial) valence bands to compare the magnitude of the response. Also, the shift current with no doping effect is included. It can be appreciated that both types of doping produces a new intense peak in the low frequency range of the spectrum. However, when \( \mu \) is situated around the nodal features of the conduction bands - around 0.5 eV above the original Fermi level - the magnitude of this peak is greatly enhanced by around an order of magnitude (the maximum value reaches \( \approx 746 \mu A/V^2 \) at \( 74 \) meV which stays outside the graph scale). The former entails that the nontrivial bands and their associated nontrivial nodal points are participating in the amplification of the current. This gives monolayer PdSe\(_2\) the potential to be used as a material for energy harvesting \([41]\). For the second response we calculated the frequency-dependent spin Hall conductivity (SHC) for different values of the chemical potential, and we report the real part in Fig.4 b). Only the usual component with spin along the \( z \) direction, and transverse current with respect to the applied external field is presented. In this case the topological character is not crucial for an enhanced magnitude of the effect, as can be checked by the large static SHC in Pt \([44]\). Also many works have reported sizable values for the two-dimensional semiconductors \([45, 46]\). For monolayer PdSe\(_2\) it is observed that the chemical potential location yields a similar trend as in the shift current case, enhancing the response. When \( \mu \) is within the range of the nodal points the SHC grows, giving additional support to the nontrivial character of the bands. It is important to note that the above-mentioned optical effects could be affected by the inclusion of quasi-particles effects, such as the discussed in \([17]\) for the linear optical response.

Additionally, from Fig. 4 b) it can be observed that the static limit (\( \omega \rightarrow 0 \)) of the optical SHC yields a nonzero value even for the system with no doping, implying a nonzero SHC within the fundamental gap. This situation has been encountered in previous calculations of the SHC on semiconductors such as in \([47, 48]\), where they mention that this in-gap SHC could not give rise to spin accumulation for trivial systems. Recently in \([46]\), it is argued that this SHC is only a numerical artifact due to the use of a broadening factor and, using degenerate perturbation theory, they obtain zero in-gap conductivities for trivial insulators. For completeness we have computed this static SHC for monolayer PdSe\(_2\), using the method of ref. \([46]\) as implemented in \([49]\), and also with the Wannier90 code \([25]\), which uses the standard broadening factor. In both cases we obtain a constant nonzero value along both the trivial and the nontrivial gap. Yet, the magnitude in the case of the trivial gap is low and in principle could not be detectable. This static SHC is presented in the SI.

**Conclusion** - In this work we complement previous works on monolayer PdSe\(_2\) by accounting for the electronic band topology of the material. We have showed that, although the valence bands of the material are trivial and in principle the systems is a trivial topological
FIG. 4. a) Shift current tensor $\sigma_{yyy}$ as a function of external photon energy for different chemical potential values. b) Spin Hall conductivity $\sigma_{xy}$ as a function of external photon energy for different chemical potential values.
ppse2, Applied Physics Letters 107, 153902 (2015).

[17] A. V. Kuklin and H. Ågren, Quasiparticle electronic structure and optical spectra of single-layer and bilayer ppse₂: Proximity and defect-induced band gap renormalization, Phys. Rev. B 99, 245114 (2019).

[18] A. V. Kuklin, L. V. Begumovich, L. Gao, H. Zhang, and H. Ågren, Point and complex defects in monolayer ppse₂: Evolution of electronic structure and emergence of magnetism, Phys. Rev. B 104, 134109 (2021).

[19] W. Lei, W. Wang, X. Ming, S. Zhang, G. Tang, X. Zheng, H. Li, and C. Autieri, Structural transition, metalization, and superconductivity in quasi-two-dimensional layered PdSe₂ under compression, Phys. Rev. B 101, 205149 (2020).

[20] L.-Y. Feng, R. A. B. Villalos, Z.-Q. Huang, C.-H. Hsu, and F.-C. Chuang, Layer-dependent band engineering of pd dichalcogenides: a first-principles study, New Journal of Physics 22, 053010 (2020).

[21] P. Giannozzi, O. Baseggio, P. Bonfia, D. Brunato, R. Car, I. Carmineo, C. Cavazzoni, S. de Gironcoli, P. Delugas, F. Ferrari Ruffino, A. Ferretti, N. Marzari, I. Timrov, A. Urru, and S. Baroni, Quantum espresso toward the exascale, The Journal of Chemical Physics 152, 154105 (2020).

[22] A. A. Mostofi, J. R. Yates, G. Pizzi, Y.-S. Lee, I. Souza, J. Ibañez-Azpiroz, S. S. Tsirkin, and I. Souza, J. Qiao, J. Zhou, Z. Yuan, and W. Zhao, Calculation of electronic structure and optical spectra of single-layer and bilayer pdse₂, Applied Physics Letters 107, 154105 (2015).

[23] A. P. C. Christopher Bradley, The Mathematical Theory of Symmetry in Solids: Representation Theory for Point Groups and Space Groups, Oxford Classic Texts in the Physical Sciences (Oxford University Press, Oxford, New York, 2010).

[24] L. Elcoro, B. Bradlyn, Z. Wang, M. G. Vergniory, J. Cano, C. Felser, B. A. Bernevig, D. Orobengoa, G. de la Flor, and M. I. Aroyo, Double crystallographic groups and their representations on the Bilbao Crystallographic Server, Journal of Applied Crystallography 50, 1457 (2017).

[25] L. Fu and C. L. Kane, Topological insulators with inversion symmetry, Phys. Rev. B 76, 045302 (2007).

[26] M. Iraola, J. L. Mañés, B. Bradlyn, T. Neupert, M. G. Vergniory, and S. S. Tsirkin, Irrep. symmetry eigenvalues and irreducible representations of ab initio band structures (2020), arXiv:2009.01764 [cond-mat.mtrl-sci].

[27] M. Taherinejad, K. F. Garrity, and D. Vanderbilt, Wannier center sheets in topological insulators, Phys. Rev. B 89, 115102 (2014).

[28] A. A. Soluyanov and D. Vanderbilt, Wannier representation of f₂ topological insulators, Phys. Rev. B 83, 035108 (2011).

[29] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, Electronics and optoelectronics of two-dimensional transition metal dichalcogenides, Nature Nanotechnology 7, 699 (2012).

[30] A. M. Cook, B. M. Fregoso, F. de Juan, S. Coch, and J. E. Moore, Design principles for shift current photovoltaics, Nat Commun 8, 14176 (2017).

[31] F. Flicker, F. de Juan, B. Bradlyn, T. Morimoto, M. G. Vergniory, and A. G. Grushin, Chiral optical response of multifold fermions, Phys. Rev. B 98, 155145 (2018).

[32] Q. Xu, Y. Zhang, K. Koepernik, W. Shi, J. van den Brink, C. Felser, and Y. Sun, Comprehensive scan for nonmagnetic Weyl semimetals with nonlinear optical response, npj Comput Mater 6, 32 (2020).

[33] G. Y. Guo, S. Murakami, T.-W. Chen, and N. Nagaosa, Intrinsic spin hall effect in platinum: First-principles calculations, Phys. Rev. Lett. 100, 096401 (2008).

[34] L. Matthes, S. Küffner, J. Furthmüller, and F. Bechstedt, Intrinsic spin hall conductivity in one-, two-, and three-dimensional trivial and topological systems, Phys. Rev. B 94, 085410 (2016).

[35] J. Slawinska, F. T. Cerasoli, H. Wang, S. Postorino, A. Supka, S. Curtarolo, M. Fornari, and M. B. Nardelli, Giant spin hall effect in two-dimensional monochalcogenides, 2D Materials 6, 025012 (2019).

[36] G. Y. Guo, Y. Yao, and Q. Niu, Ab initio calculation of the intrinsic spin hall effect in semiconductors, Phys. Rev. Lett. 94, 226601 (2005).

[37] Y. Yao and Z. Fang, Sign changes of intrinsic spin hall effect in semiconductors and simple metals: First-principles calculations, Phys. Rev. Lett. 95, 156601 (2005).

[38] F. Cerasoli, M. B. Nardelli, M. Costa, S. Curtarolo, R. D. Gennaro, M. Fornari, L. S. I. Liyanage, A. R. Supka, and H. Wang, Paoflow: A utility to construct and operate on
ab initio hamiltonians from the projections of electronic wavefunctions on atomic orbital bases (pao), including characterization of topological materials, Bulletin of the American Physical Society \textbf{2018} (2018).

[50] S. Haastrup, M. Strange, M. Pandey, T. Deilmann, P. S. Schmidt, N. F. Hinsche, M. N. Gjerding, D. Torelli, P. M. Larsen, A. C. Riis-Jensen, J. Gath, K. W. Jacobsen, J. Jørgen Mortensen, T. Olsen, and K. S. Thygesen, The Computational 2D Materials Database: high-throughput modeling and discovery of atomically thin crystals, 2D Mater. \textbf{5}, 042002 (2018).

[51] K. Choudhary, I. Kalish, R. Beams, and F. Tavazza, High-throughput Identification and Characterization of Two-dimensional Materials using Density functional theory, Scientific Reports \textbf{7}, 5179 (2017), number: 1 Publisher: Nature Publishing Group.