2D Materials

Landau levels in 2D materials using Wannier Hamiltonians obtained by first principles

J L Lado¹ and J Fernández-Rossier¹,²

¹ International Iberian Nanotechnology Laboratory (INL), Av. Mestre José Veiga, 4715–330 Braga, Portugal
² Departamento de Física Aplicada, Universidad de Alicante, E-03690 San Vicente del Raspeig, Spain

E-mail: jose.luis.lado@gmail.com

Keywords: Landau levels, quantum Hall, density functional theory, Wannier functions, Dirac-ness

Abstract

We present a method to calculate the Landau levels and the corresponding edge states of two dimensional (2D) crystals using as a starting point their electronic structure as obtained from standard density functional theory (DFT). The DFT Hamiltonian is represented in the basis of maximally localized Wannier functions. This defines a tight-binding Hamiltonian for the bulk that can be used to describe other structures, such as ribbons, provided that atomic scale details of the edges are ignored. The effect of the orbital magnetic field is described using the Peierls substitution in the hopping matrix elements. Implementing this approach in a ribbon geometry, we obtain both the Landau levels and the dispersive edge states for a series of 2D crystals, including graphene, Boron Nitride, MoS2, Black Phosphorous, Indium Selenide and MoO3. Our procedure can readily be used in any other 2D crystal, and provides an alternative to effective mass descriptions.

1. Introduction

The motion of electrons in two dimensions under the influence of a perpendicular magnetic field $B$ results in a discrete spectrum of energy levels, associated to the bound closed cyclotron orbits expected within the classical picture. In the case of Schrödinger electrons, the discrete spectrum was first calculated by Landau [1], that showed that $E_n = \hbar \omega_0 \left( n + \frac{1}{2} \right)$, where $n = 0, 1, \ldots$ are integer numbers and $\hbar \omega_0 = eB/m$, where $e$ and $m$ are the charge and mass of the electron. The concept of Landau levels (LL) is also useful in systems for which the effective mass approximation is a good description of the relevant energy bands, such as semiconductor two dimensional (2D) electron gases [2]. With the observation of the unconventional quantum Hall effect in graphene [3, 4], it was soon realized that the spectrum of quantized levels was different from the usual Landau quantization, and they would rather scale as $E_n = \text{sgn}(n) n \nu_F \sqrt{2e\hbar B |n|}$, with $n = 0, \pm 1, \pm 2, \ldots$ and $\nu_F$ being the Fermi velocity of graphene carriers. This unconventional spectrum of LL can easily be obtained using the kp effective mass Hamiltonian for graphene, isomorphic to the celebrated Dirac Hamiltonian.

The physics of the magnetic quantum oscillations [5–7] and, in the extreme quantum limit, the quantum Hall effect of a given system, are often best described in terms its LL. The quest for samples with increased mobility has finally led to the observation of the quantum Hall effect in few layer black phosphorous [8], in thin film transition metal disulfides [9] and monolayer WSe2 [10] which provides an experimental motivation for this work. Importantly, the properties of LL can be dramatically different depending on the symmetry of the crystal. Thus, hexagonal crystals such as graphene [11] and MoS2 [12] have LL that can be accounted for in terms of two sets of Dirac electrons, one per valley, whereas in the case of black phosphorous the spectrum is similar to the more conventional case of Schrodinger LL [13, 14]. Dirac LL are dramatically different from Schrodinger LL, as they come in three groups, electron-like, hole-like and the intriguing 0 Landau level. Whereas electron and hole Dirac-LL have a twofold valley degeneracy, the 0 LL breaks valley symmetry.

The conventional procedure to calculate the quantized levels of electrons in 2D systems, either quantum wells or 2D crystals, requires to derive the right kp effective mass Hamiltonian [15, 16], and solve the Schrodinger equation, replacing $\mathbf{p}$ by $\mathbf{p} - A$.
The effective mass approximation is well suited for this task because the magnetic length \( l_B = \sqrt{\frac{\hbar}{eB}} = 25 \text{ nm} / \sqrt{\text{Tesla}} \) is much larger than the crystal period for laboratory scale magnetic fields. When applied to an infinite 2D system without edges, this approach yields a set of dispersion-less LL, very often after a simple analytic calculation. The determination of the dispersive edge states requires to solve the equation without translational invariance in the direction perpendicular to the edge \([17, 18]\), which normally requires numerical solution.

The implementation of the kp method can become impractical in some situations, such as in-plane heterojunctions of 2D crystals, or in general, whenever the kp Hamiltonian for bulk is not known. In these situations, the calculation of both the bulk LL and the edge states could be done if a tight-binding Hamiltonian for the system is known. In that case, the effect of the magnetic field is included by doing the so called Peierls substitution \([15]\), that consists in replacing the hopping \( t_{i,j} \) by \( t_{i,j} e^{i\Phi_{i,j}} \), where \( \Phi_{i,j} = \frac{e}{\hbar} \int_{\gamma_{i,j}} A \cdot dl \) is the circulation of the vector potential \( A \) associated to the magnetic field. This strategy is very often used in the case of graphene, for which a straightforward tight-binding Hamiltonian is available \([19]\), and permits to compute the edge states, as well as interface states in the case of in-plane heterojunctions \([20]\). However, tight-binding models are not always available.

Here we propose a constructive approach to obtain both the quantized levels, edge states and interface states valid for a very wide variety of 2D crystals and Van der Waals heterostructures. Our strategy consists in deriving a tight-binding Hamiltonian for a given 2D crystal starting from DFT calculations, using the well tested Wannierization method \([21–26]\). This procedure allows to obtain an exact representation of the DFT Hamiltonian in a basis set of localized orbitals, i.e., a tight-binding representation \([27–31]\). This procedure is carried out in the absence of magnetic field and yields a tight-binding description that captures the topology and orbital weight of the states in the whole Brillouin zone, as opposed to being valid close to high symmetry points, giving thereby an accurate description for complex materials. Once this is done at \( B = 0 \), the addition of the effect of the magnetic field using the Peierls substitution is straightforward and permits to obtain both the LL and the edge states, provided electronic reconstructions triggered by magnetic field are not considered.

2. Methods

The Wannierization procedure consists in a change of basis, from the Bloch basis \( |\mathbf{k}, \mathbf{i}\rangle \) which are eigenstates of the Kohn Sham Bloch Hamiltonian \( H_{\text{KS}}(\mathbf{k}) |\mathbf{k}, \mathbf{i}\rangle = \epsilon_{\mathbf{k},\mathbf{i}} |\mathbf{k}, \mathbf{i}\rangle \), into a localized Wannier basis \( |\mathbf{n}, \nu\rangle \). Here \( \nu \) stands for band index. The change of basis is performed by an integration of the Bloch waves in the whole Brillouin zone, weighted by a gauge field \( U(\mathbf{k})_{\mathbf{i},\nu} \), so that

\[
|\mathbf{n}, \nu\rangle = \frac{1}{\sqrt{V}} \int d\mathbf{k} e^{i\mathbf{k} \cdot \mathbf{r}} U(\mathbf{k})_{\mathbf{i},\nu} |\mathbf{k}, \nu\rangle.
\]

In particular, the change of basis is characterized by the unitary field \( U(\mathbf{k})_{\mathbf{i},\nu} \), which is chosen so that the Wannier orbitals have the smallest spread in real space, giving rise to the so-called maximally localized Wannier functions \([21, 25]\). The Hamiltonian in the Wannier basis is no longer diagonal, but due to the localized nature of Wannier states, it only couples states whose positions are close in real space, giving rise to a sparse Hamiltonian. This procedure is performed in the set of bands relevant for the low energy properties, giving rise to a Hamiltonian with a size much smaller than the original DFT one, but reproducing the Hamiltonian in the energy window of the Wannierized bands.

Due to the small matrix size of the Wannier Hamiltonian, it is possible to precisely calculate quantities that depend strongly on the number of k-points. This procedure has been successfully applied (among others) to calculate optical \([32]\), thermoelectric \([33]\), ballistic transport \([24]\) and strong correlations through dynamical mean field theory \([34]\). Here we are interested in the calculation of LL and edge states in 2D crystals and, as we discuss now, the DFT calculation is done for the unit cell of the bulk 2D crystal. The obtained Wannier Hamiltonian represents a 2D tight binding model and has the following form

\[
H_{2D} = \sum_{n,m,i,j} t_{ij}^{n-m} \epsilon_{n,i}^\dagger \epsilon_{m,j}
\]

which in reciprocal space reads

\[
H_{2D}(\mathbf{k}) = \sum_{n,m,i,j} e^{i\mathbf{k} \cdot (\mathbf{r}_n - \mathbf{r}_m)} t_{ij}^{n-m} \epsilon_{n,i}^\dagger \epsilon_{m,j}
\]

where \( i, j \) are the indexes of the different orbitals in the unit cell and \( n, m \) are the vectors that label the different unit cells. The matrices \( t_{ij}^{n-m} \) are the hoppings between the Wannier orbitals between the different unit cells

\[
t_{ij}^{n-m} = \langle \mathbf{n}, i | H_{\text{KS}} | \mathbf{m}, j \rangle
\]

with \( |\mathbf{n}, i\rangle \) the ith Wannier orbital in the cell \( \mathbf{n} \). In figure 1(b) it is shown a sketch of the meaning of those matrices in real space, for the case of a square lattice and hopping to first neighboring cells.

Once we have the hopping integrals equation (3), obtained for the minimal unit cell that describes the 2D crystal, we can build a model for a one dimensional slab, as schematically shown in figure 1(c). In the same step it is also possible to add the effect of the magnetic field acting on the orbital degrees of freedom using the Peierls substitution. Assuming that the bar is infinite in the x direction, we use the Landau gauge \( A = (By, 0, 0) \) that maintains the translation symmetry of the Hamiltonian, and modifies the hoppings \( t_{ij}^{n-m} \) of the 1d unit cell according to...
where

\[ \phi^{N,M}_{ij} = \frac{eB}{2\hbar}(x_i^N - x_j^M)(y_i^N + y_j^M) \]

(5)

is the Peierls phase, \( B \) the magnetic field and \( x_i^N, y_i^N, x_j^M, y_j^M \) the center of the different Wannier orbitals in the cells \( N \) and \( M \) of the 1d system. Finally, by calculating the expectation value of the position along the width of the ribbon for each state, we obtain whether a certain state is a bulk LL or an edge state (see figure 1(d)).

Since the method uses the same matrix elements for edge and bulk atoms, it completely misses the atomic scale reconstructions at the edges, such as dangling bonds and any other edge specific atomic scale process. The method assumes that the edges are identical to bulk, except for the reduced coordination. Whereas this assumption is certainly not realistic to describe atomic scale edge properties, it provides a quite reliable description of both bulk LL and even the edge states associated to propagating modes along the boundaries of the sample, whose localization length along the transverse direction is given by \( l_B \), much larger than the lattice constant.

\[ f^{ij} \to f^{ij} e^{i\phi^{N,M}_{ij}}, \]  

(4)

3. Results

3.1. Graphene

We now test the procedure with graphene [19]. In a single graphene layer, the low energy properties are dominated by two \( p_z \)-like orbitals, one in each carbon atom. At higher energies, the decoupled \( p_z \) bands coexist with bonding/antibonding \( sp^2 \) states. To perform the Wannierization, a frozen window of \([-1, 1] eV\) is chosen so it contains the low energy region, whereas the outer window goes up to \([0, +9] eV\) to capture the whole \( p_z \) manifold. The comparison between the full DFT band structure and the Wannier band structure is shown in figure 2(a). It is apparent that the Wannierization captures both the low energy Dirac dispersion as well as the electron hole asymmetry which arises due to second neighbor hopping [35].

Upon application of a magnetic field in a ribbon build with the previous Hamiltonian, the familiar set of Dirac LL appear. In particular (figure 2(b)), a single zero Landau level per valley shows up, that connects with zigzag edge states which show some dispersion due to the \( finite \) second neighbor hopping [35]. Except for this feature, associated to states atomically localized at the edges, the method yields results identical to those obtained with the standard tight-binding model.
The color of the bands in figure 2(b) shows the spatial location of the state: green stands for bulk, whereas red and blue stand for top and bottom edge respectively. We can repeat the calculation for several values of $B$ and study the evolution of the LL spectra as a function of $B$. We obtain the expected square root behavior of the energy with $B$. Independently on the magnetic field the first LL is always pinned at zero energy and two fold degenerate, originating one from each valley. Finally, the evolution of the LL energy for a fixed magnetic field as a function of the LL index can be obtained in the same way, showing the expected square root behavior. This further confirms the reliability of our method.

### 3.2. Boron nitride (BN)

Hexagonal BN [36, 37] is a 2D material which is mostly known for its insulating behavior and its extraordinary properties for acting as a high quality substrate for other 2D materials [38–41]. Very much like graphene, BN consist on a honeycomb lattice, but with two inequivalent atoms, boron and nitrogen, in the unit cell. Its electronic structure is usually understood as a gapped Dirac equation in the $p_z$ manifold, having a direct band gap, although recent findings suggest that its bulk form shows an indirect gap [42].

The electronic structure obtained with DFT is shown in figure 3(a), as well as the comparison with the bands obtained via Wannierization with $p_z$-like orbitals of boron and nitrogen. The low energy properties show a strong electron–hole asymmetry, giving rise in the conduction to a quite flat band between $K$ and $K'$, so that in the following we will focus on the more conventional valence band. In figure figure 3(b) we show the LL obtained with the Wannier Hamiltonian, focusing on the valence band. It is apparent that the spectrum is different for $K$ and $K'$ valleys (positive and negative values of $k$ in the figure), as expected for the case of a massive Dirac equation [43]. In particular, the $n = 0$ LL for holes is only present in one of the valleys. The scaling of the LL with the magnetic field is shown in figure 3(c), where it is observed the flatness with $B$ of the 0LL, expected in a massive Dirac equation [43] and the almost linear dispersion of the LL with $B$, expected for Dirac electrons with a large mass.

### 3.3. MoS$_2$

Transition metal dichalcogenides (TMD) are another set of materials that can be exfoliated into 2D flakes and are attracting enormous interest [44]. They also have a hexagonal structure, but their electronic structure is more complicated than the one of graphene and BN, involving several $d$ orbitals of the transition metal, and also some contribution coming from the $p$ orbitals of the group VI atom [27]. Therefore, obtaining a Slater Koster model or a tight binding model by fitting to the band structure is a very
A challenging task [45–50]. Even if a good fitting is obtained, the fact that the parametrized Hamiltonian reproduces the topology and orbital character of the original Hamiltonian has to be carefully checked. In contrast, the Wannierization procedure allows to get the tight binding Hamiltonian in a single shot, reproducing both the topology and orbital weights of the bands.

Unconventional Hall effect in dichalcogenides [12, 51, 52] is expected due to the Dirac-like nature of its band structure [53]. In the following, we will focus on the case of MoS₂, although a similar analysis can be applied to other transition metal TMD. We study first the conduction band, for which the effect of spin–orbit coupling is much smaller [27] than in the valence band, so that it can be initially neglected. In particular, the spin–orbit splitting in the conduction band is much smaller than the LL splitting for moderate values of $B$. For the particular case of MoS₂, the orbitals chosen as initial guess are the p orbitals in S and the d-orbitals in Mo, giving rise to a 11 band Hamiltonian [27].

The comparison between the DFT and Wannier Hamiltonians obtained is shown in figure 4(a). We emphasize that since the Wannierization is simply a change of basis, the orbital information is perfectly conserved between the DFT Kohn Sham states and the tight binding Hamiltonian. With the previous Hamiltonian a quantum Hall slab can be built, that permits to compute the Landau level spectra shown in figure 4(b). Because of the lack of inversion symmetry, the $n = 0$ Landau level in the conduction band is only present in one valley as observed in figure 4(b) [54, 55]. In addition, for Landau indexes $n > 0$, a sizable valley splitting has been predicted [52, 54, 56], based on a three band tight binding model, feature that would not be observed in the LL of a massive Dirac equation. Including hopping up to third neighboring cells, we find that the valley splitting in the conduction band is rather small. In comparison, if we only retain hopping to the first neighboring cell, we recover the sizable intervalley splitting predicted [54, 56]. We thus conclude that the $n > 0$ valley splitting in the conduction band depends strongly on the details of the tight binding Hamiltonian used.

So far we have ignored the effect of spin–orbit coupling. We can implement the method used so far starting from a DFT calculation that includes spin–orbit coupling, and performing a Wannierization over a fully relativistic calculation. The results of this procedure are shown in figure 5(a), and the LL for the valence band in a quantum Hall slab are shown in figure 5(c).

Nevertheless, the effect of SOC can also be captured without a fully relativistic Wannierization, but just by adding an atomic-like SOC term to the spinless Wannierization performed previously [27]. This will be valid as long as the Wannier orbitals are atomic-like close to the atom [27, 57] (which is where the SOC has its strongest contribution), and provided the SOC...
splitting comes from the manifold where the Wannierization was performed. For example, in the case of graphene, the first principles SOC gap of 40 μeV will be reproduced with the previous procedure only if the Wannierization includes d-orbitals of carbon [58, 59], whereas only inclusion of sp orbitals would yield a gap.
1 μeV for realistic SOC coupling.\textsuperscript{[60, 61]} much below the actual DFT value.

The inclusion of SOC after the Wannierization gives rise to the following Hamiltonian

\[ H = H_{\text{spinless}} + H_{\text{SOC}} \]  

where

\[ H_{\text{SOC}} = \sum_{a \in \text{atoms}} \lambda_a \sum_{i,j \leq d} (\mathbf{L} \cdot \mathbf{S}) \epsilon_{ij}^d \epsilon_{ij'}^d \]  

is the atomic spin–orbit coupling. \( H_{\text{spinless}} \) is the Wannier Hamiltonian obtained from the non relativistic DFT calculation, for the bulk or the ribbon depending on the case.

This procedure avoids having to perform a relativistic calculation, and can be useful to approximately capture SOC effects if a particular DFT code lacks of relativistic implementation, if the fully relativistic calculation is computationally too expensive, or simply to study how the band structure evolves as the SOC is turned on\textsuperscript{[27]}. It is important to note that effects produced by variations of the DFT charge density by SOC effects will not be captured, so that small differences in dispersions and effective masses are expected.

The values of \( \lambda_{\text{Mo}} \) and \( \lambda_{\text{S}} \) in equation (7) correspond approximately to the atomic SOC in Mo and S, which was shown\textsuperscript{[27]} to be on the order of 80 meV for Mo and 50 meV for S. The bulk band structure obtained with the non relativistic Wannierization plus atomic SOC following equation (7) is shown in figure 5(b). It is observed that this method gives a band structure in good agreement with the fully relativistic one (figure 5(a)), in particular reproducing the valley spin splitting in the \( K \) and \( K' \) points. The quantum Hall effect in this particular system is shown in figure 5(c) for the fully relativistic Wannierization and in figure 5(d) for the non-relativistic Wannierization plus atomic SOC. In both cases it is observed that due to the large spin splitting in the valence valleys, the LL are spin polarized for each valley, and with a valley-dependent spectrum for the values of the Landau index larger than 0. More importantly, only one of the valleys shows a single Landau level, which turns the system into a quantum spin ferromagnet upon hole doping. Although methods 5(c), (d) give qualitative similar results, a small difference in effective mass between both calculations create a small misalignment between the levels.

Finally, it is worth to note that the previous calculations do not include nor the Zeeman term \( H_z = 2\mu_B \mathbf{B} \cdot \mathbf{S} \) neither the coupling to the atomic orbital angular momentum \( H_K = \mu_B \mathbf{B} \cdot \mathbf{L} \), where \( \mathbf{L} \) is the atomic angular momentum, \( \mathbf{S} \) the spin, and \( \mu_B \) the Bohr magneton. This orbital coupling is internal and it is different from the orbital magnetization\textsuperscript{[62–64]}. In the case of MoS\textsubscript{2}, the last angular term would create a valley dependent splitting in the valence band that increases linearly with \( B \), since the states in the valence band valleys are dominated by \( L_z = \pm 2 \) from Mo. In comparison, its contribution in the conduction band will be much smaller, due to the \( L_z = 0 \) dominant character. The Zeeman term would create a spin splitting in both valleys, whose effect would be more important in the conduction band, where at large enough fields would be able to compete with the small SOC splitting of the conduction band.

### 3.4. Black phosphorus, InSe and MoO\textsubscript{3}

In the following we will apply the method presented to other semiconducting 2D materials. In particular we will study cases whose low energy properties are believed to be dominated by Schrodinger-like dispersion relations, rather than Dirac like.

We first turn our attention to monolayer black phosphorus\textsuperscript{[65]}, a 2D semiconductor that shows highly anisotropic electronic properties due to its distorted lattice. Its a direct gap semiconductor, with top of the valence and bottom of the conduction bands located at the \( \Gamma \) point in the Brillouin zone.

The strong mixing between \( s \) and \( p \) orbitals in black phosphorus, together with the low symmetry of the unit cells turns the fitting of its electronic structure a very challenging task if few orbitals are considered\textsuperscript{[66–68]}. In order to properly capture the electronic structure of black phosphorus, we carry out the Wannierization with 16 Wannier orbitals, corresponding to the \( s \) and \( p \) orbitals of the four atoms of the unit cell. The inclusion of all those orbitals gives rise to a tight binding model that agrees well with the DFT eigenvalues as shown in figure 6(a). The Wannierization with the 16 orbitals is not computationally expensive, and importantly its construction in this way warrants that all the orbital weights are properly captured.

Implementing this Hamiltonian in a one dimensional black phosphorus slab, and using the Peierls substitution, we obtain the spectrum of LL\textsuperscript{[69]} and edge bands shown in figure 6(b). The anisotropic nature of the low energy properties averages out\textsuperscript{[13, 69]}, and the resulting scaling with the LL index (figure 6(d)) and magnetic field (figure 6(c)) are in line with those obtained using the effective mass approach\textsuperscript{[13]}.

We now implement our method for a monolayer of indium selenide\textsuperscript{[70]}, another semiconductor that can synthesized in 2D form. It shows a hexagonal lattice, very much like TMD, but with four atoms per unit cell instead of three, two In and two Se\textsuperscript{[70–72]}. It has an indirect gap between the conduction band at \( \Gamma \) and a Mexican hat around \( \Gamma \) in valence\textsuperscript{[70]}, with a direct gap of similar value. The gap is in the order of 1.6 eV, and tunable by a perpendicular electric field\textsuperscript{[70]}. In addition, electroluminescence\textsuperscript{[73]} as well as by confinement effects\textsuperscript{[74]} have been recently experimentally observed.

For the sake of simplicity, in the following we focus on the conduction band of InSe, that shows a minimum at \( \Gamma \). The lack of inversion symmetry will create a
spin splitting in the band structure once SOC is considered, that vanishes at the Γ point, a time reversal invariant momenta. With that in mind, we perform a non relativistic calculation, together with the Wannierization (figure 7(a)) of the InSe monolayer. The Wannierization is performed using 14 orbitals, s and p
of In and p of Se (each unit cell has 2 Se and 2 In). With the Wannier Hamiltonian, the Hall bar is created (figure 7(b)), giving rise to a conventional LL spectra. The scaling of the LL energy with the magnetic field (7(c)) and with the Landau index (7(d)) is the one of the conventional 2d electron gas. Therefore, the conduction band of InSe is one of the cleanest examples of Schrodinger dispersion in a 2d material, lacking of SOC splitting or Berry curvature effects. In striking comparison, the valence band will show both SOC effects and Berry curvature effects, since the top of the valence band is not at $\Gamma$.

The last 2D material we consider is MoO$_3$ [75] another semiconducting material that can be brought to 2D form[76], giving rise to a bilayer system formed by two Mo planes. It has an orthorhombic unit cell, with each Mo atom sitting in an octahedral environment of O atoms. It is an indirect gap semiconductor, even in the 2D form, with a gap between the conduction band at $\Gamma$ and the valence band at $M$[76].

The low energy properties of this compound can be captured taking into account the d orbitals of Mo and the p orbitals of O, giving rise to $28 \times 28$ tight binding Hamiltonian. In the following, we will focus on the LL of the valence band, which corresponds to the parabolic band located at $M$. At that point, two bands coexist, which correspond to the two different Mo layers in the unit cell, each one giving rise to one set of LL. The MoO$_3$ LL spectrum, shown in figure 8(b), is the one expected for Schrodinger quasiparticles, except for the twofold orbital degeneracy associated to the layer index. The degeneracy remains as we ramp the magnetic field (figure 8(c)), and for the different Landau indexes (figure 8(d)). The degeneracy could be lifted upon application of a perpendicular electric field or, more interestingly, if electronic order arises due to electron–electron interaction.

4. LL as a measure of Dirac-ness

We now brieﬂy discuss the concept of Dirac-ness and we use a recently proposed method to quantify it [77]. There is no doubt that quasiparticles in graphene behave as Dirac electrons. However, when a given 2D crystal has a gap, things are less clear as the energy dispersion of two Schrodinger bands is very similar to the spectrum of a gapped Dirac equation. A simple way to measure the Dirac-ness of a band structure consists on looking at the evolution of the zero LL with magnetic field [77]. This idea is based on the fact that for Schrodinger fermions, the energy of the LL follow

$$E_n = \Delta + \left(\frac{\hbar e B}{m}\right) n$$

whereas for Dirac massive fermions in the large mass regime $E_n \approx \Delta + \left(\frac{\hbar e B}{m}\right) n$, where $\Delta$ in the energy off-set of the band and $m$ the effective mass. The previous expression can be generalized into

$$E_n = \Delta + \left(\frac{\hbar e B}{m}\right) (n + \gamma)$$

Figure 8. (a) Comparison of the band structure of monolayer MoO$_3$ as obtained by DFT and the Wannier tight binding Hamiltonian, showing a maximum in the valence band at $M$, with two spinless degenerate bands. (b) Band structure of MoO$_3$ nanoribbon of 40 nm thickness in the quantum Hall regime ($B = 115$ T), focusing on the valence band, showing a conventional Landau level spectra. (c) Scaling of the Landau levels energy with the magnetic field, and with the Landau index (d) at a fixed magnetic field, showing that the two sets of Landau levels are degenerate in energy. Ribbon thickness in (c),(d) is 160 nm.

2D Mater. 3 (2016) 035023 J Lado and J Fernández-Rossier
with $\gamma = 0$ for Dirac and $\gamma = 1/2$ for Schrodinger. Therefore, a key feature of massive Dirac fermions is that the energy of the zero LL is independent of the magnetic field, showing a flat evolution of the LL energy versus magnetic field. On the contrary, conventional Schrodinger fermions will have all their LL dependent on the magnetic field, so that no flat evolution is observed.

The Dirac-ness can be easily observed by checking the LL versus magnetic field as obtained for the different materials. In particular, graphene (figure 2(c)), boron nitride (figure 3(c)) and MoS$_2$ (figure 4(c)) show a zero LL whose energy is independent of the magnetic field, and thereby they are Dirac materials. In contrast, black phosphorus (figure 6(c)), InSe (figure 7(c)) and MoO$_3$ (figure 8(c)) show a first Landau level with non-zero slope. By fitting the first four LL at the different magnetic fields shown in figures 2–4, 6–8: to equation (8), we obtain the values shown in table 1.

### 5. Conclusions

We have shown that using the Wannierization procedure a faithful tight-binding representation of the DFT Hamiltonian can be obtained for several 2D materials. We have shown how the addition of a Peierls phase into the Wannier Hamiltonian permits to compute the LL spectrum, both for bulk and edge states, of a variety of 2D materials, including graphene, BN, MoS$_2$, black phosphorous, Indium Selenide and MoO$_3$. The method is particularly suitable for systems lacking a reliable tight-binding model, or for which the derivation of an effective mass kp Hamiltonian is complicated or not available. We have also shown that by analyzing the evolution of the LL spectra, the Dirac-ness of the band structure can be determined, yielding a simple tool to identify materials with Dirac physics.

### Acknowledgments

JFR acknowledges financial support by MEC-Spain (FIS2013–47328-C2-2-P) and Generalitat Valenciana (ACOMP/2010/070), Prometeo. This work has been financially supported in part by FEDER funds. We thank B Amorim and N García-Martínez for fruitful discussions. We acknowledge financial support by Marie-Curie-ITN 607904-SPINOGRAPH. JL Lado thanks the hospitality of the Departamento de Física Aplicada at the Universidad de Alicante. This work was supported by National Funds through the Portuguese Foundation for Science and Technology (FCT) in the framework of the Strategic Funding UID/FIS/04650/2013 and through project PTDC/FIS-NAN/3668/2014.

### Appendix. Computational details

The starting point is density functional calculations, performed with Quantum Espresso, for the unit cell of the desired 2D crystal. We use PBE [78] functional and the PAW pseudopotentials [79] for structural relaxation. Wannierization [21–25] is performed in $20 \times 20 \times 1$ kmesh, over the non relativistic calculation with PAW pseudopotentials, except for the case of relativistic MoS$_2$ where we used norm conserving pseudopotentials. With the Wannier Hamiltonian for bulk, the tight binding Hamiltonian for the ribbon is created by taking the relevant tight binding parameters of the bulk Hamiltonian for each cell replica, considering hoppings up to third neighboring cells.

The scaling of the LL with magnetic field is calculated first by determining the position in reciprocal space of the flat Landau bands (in the case of graphene, BN and MoS$_2$ two different regions). The diagonalization of the quantum Hall slab is performed in that kpoint, retaining only those eigenvalues whose eigenfunctions are located in the bulk to throw away edge states and dangling bond eigenvalues (see figures 4(b), 7(b)). This procedure allows to study very wide ribbons, since the tight binding Hamiltonian is highly sparse and a few eigenvalues around the Fermi energy can be efficiently calculated with ARPACK [80].

### References

[1] Landau L and Lifshitz E 1962 Quantum Mechanics (Non-Relativistic Theory) Course on Theoretical Physics vol 3 (Oxford: Pergamon)
[2] Ando T, Fowler A B and Stern F 1982 Electronic properties of two-dimensional systems Rev. Mod. Phys. 54 437–672
[3] Novoselov K, Geim A K, Morozov S, Jiang D, Katsnelson M, Grigorieva I, Dubonos S and Firsov A 2005 Two-dimensional gas of massless dirac fermions in graphene Nature 438 197–200
[4] Zhang Y, Tan Y-W, Stormer H L and Kim P 2005 Experimental observation of the quantum Hall effect and Berry’s phase in graphene Nature 438 201–4
[5] Gillgren N et al 2014 Gate tunable quantum oscillations in air-stable and high mobility few-layer phosphorene heterostructures 2D Mater. 2 101001
[6] Li L et al 2015 Quantum oscillations in a two-dimensional electron gas in black phosphorus thin films Nat. Nanotechnol. 10 698–713
[7] Tayari V, Hemsworth N, Fakih I, Favron A, Gaufrès E, Gervais G, Martel R and Szokep T 2015 Two-dimensional magnetotransport in a black phosphorus naked quantum well Nat. Commun. 6 7702
[8] Li L et al 2016 Quantum Hall effect in black phosphorus two-dimensional electron system Nat. Nanotechnol. 11 593–7
[9] Wu Z 2015 Observation of valley Zeeman and quantum Hall effects at q valley of few-layer transition metal disulfides arXiv:1511.00077

[10] Fallahazad B, Movva H C P, Kim K, Larentis S, Taniguchi T, Watanabe K, Banerjee S K and Tutuc E 2016 Subnibkova: haas oscillations of high-mobility holes in monolayer and bilayer wSe2; Landau level degeneracy, effective mass, and negative compressibility Phys. Rev. Lett. 116 086601

[11] Zhang Y and Ando T 2002 Hall conductivity of a two-dimensional graphite system Phys. Rev. B 65 245420

[12] Li X, Zhang F and Niu Q 2013 Unconventional quantum Hall effect and tunable spin Hall effect in dirac materials: application to an isolated mos, trilayer Phys. Rev. Lett. 110 066803

[13] Pereira J M and Katsnelson M I 2015 Landau levels of single-layer and bilayer phosphorene Phys. Rev. B 92 075457

[14] Yuan S, Katsnelson M I and Bolda R 2015 Quantum Hall effect in biased black phosphorus arXiv:1512.06345

[15] Saito R et al 1998 Physical Properties of Carbon Nanotubes vol 35 (Singapore: World Scientific)

[16] Katsnelson M 2012 Graphene: Carbon in Two Dimensions (Cambridge: Cambridge University Press)

[17] Halperin B J 1982 Quantized Hall conductance, current-carrying edge states, and the existence of extended states in a two-dimensional disordered potential Phys. Rev. B 25 2185–90

[18] Beyr Land Fertig H A 2006 Edge states and the quantized Hall effect in graphene Phys. Rev. B 73 195408

[19] Castro Neto A H, Guinea F, Peres N M R, Novoselov K S and Geim A K 2009 The electronic properties of graphene Rev. Mod. Phys. 81 109–62

[20] Lado J, González J W and Fernández-Rossier J 2013 Quantum Hall effect in gapped graphene heterojunctions Phys. Rev. B 88 035448

[21] Marzari N and Vanderbilt D 1997 Maximally localized generalized wannier functions for composite energy bands Phys. Rev. B 56 12847–65

[22] Mostofi A A, Yates J R, Lee Y S, Souza I, Vanderbilt D and Marzari N 2008 Wannier90: a tool for obtaining maximally-localised wannier functions Comput. Phys. Commun. 178 685–99

[23] Souza I, Marzari N and Vanderbilt D 2001 Maximally localized wannier functions for entangled energy bands Phys. Rev. B 65 035109

[24] Calzolari A, Marzari N, Souza I and Buongiorno Nardelli M 2004 Ab initio transport properties of nanostructures from maximally localized wannier functions Phys. Rev. B 69 035108

[25] Marzari N, Mostofi A A, Yates J R, Souza I and Vanderbilt D 2012 Maximally localized wannier functions: theory and applications Rev. Mod. Phys. 84 1419–75

[26] Thonhauser T and Vanderbilt D 2006 Insulator/chern-insulator transition in the haldane model Phys. Rev. B 74 235111

[27] Košmider K, González J W and Fernández-Rossier J 2013 Large spin splitting in the conduction band of transition metal dichalcogenide monolayers Phys. Rev. B 88 245436

[28] Chen L, Wang Z F and Liu F 2013 Robustness of two-dimensional topological insulator states in bilayer bismuth against strain and electrical field Phys. Rev. B 87 235420

[29] Lado J and Pardo V 2016 Dirac topological insulator inthe 2d2 manifold of a honeycomb oxide arXiv:1604.05554

[30] Jung J and MacDonald A H 2013 Tight-binding model for graphene σ-bands from maximally localized wannier functions Phys. Rev. B 87 195430

[31] Huang H, Liu Z, Zhang H, Duan W and Vanderbilt D 2015 Emergence of a chern-insulating state from a semi-dirac dispersion Phys. Rev. B 92 161115

[32] Assmann E, Wissgott P, Kunej T, Tocchi A, Blaha P and Held K 2016 Wopict: optical conductivity with wannier functions and adaptive k-mesh refinement Comput. Phys. Commun. 202 1–11

[33] Pizzi G, Volja D, Kozinski B, Fornari M and Marzari N 2014 Boltzmann: a code for the evaluation of thermoelastic and electronic transport properties with a maximally-localized wannier functions basis Comput. Phys. Commun. 185 422–9

[34] Lechermann F, Georges A, Poteryaev A, Biermann S, Posternak M, Yamaski A and Andersen O K 2006 Dynamical mean-field theory using wannier functions: a flexible route to electronic structure calculations of strongly correlated materials Phys. Rev. B 74 125120

[35] Kretinin A, Yu G L, Jalil R, Cao Y, Witwers F, Mischenko A, Katsnelson M I, Novoselov K S, Geim A K and Guinea F 2013 Quantum capacitance measurements of electron-hole asymmetry and next-nearest-neighbor hopping in graphene Phys. Rev. B 88 165427

[36] Gorbachev R V et al 2011 Hunting for monolayer boron nitride: optical and raman signatures Small 7 465–8

[37] Alem N, Ern R, Kiselevsky C, Rosell M D, Gannett W and Zettl A 2009 Atomically thin hexagonal boron nitride probe by ultrahigh-resolution transmission electron microscopy Phys. Rev. B 80 155425

[38] Young A F, Sanchez-Yamagishi J, Hunt B, Choi S H, Watanabe K, Taniguchi T, Asahi R and Jarillo-Herrero P 2014 Tunable symmetry breaking and helical edge transport in a graphene quantum spin Hall state, Nature 505 528–32

[39] Gurrum M, Omar S, Zihlmann S, Makk P, Schönenberger C and van Wees B J 2016 Spin transport in fully hexagonal boron nitride encapsulated graphene Phys. Rev. B 93 115444

[40] Lee G H, Cui K, Kim Y D, Arefe G, Zhang X, Lee C H, Ye F, Watanabe K, Taniguchi T, Kim P and Hone J 2013 Highly stable, dual-gated mos, transistors encapsulated by hexagonal boron nitride with gate-controllable contact, resistance, and threshold voltage, ACS Nano 7 9019–26

[41] Britnell L 2012 Atomically thin boron nitride: a tunnelling barrier for graphene devices arXiv:1202.0735

[42] Cassabois G, Valentin P and Gil B 2015 Hexagonal boron nitride is an indirect bandgap semiconductor arXiv:1512.02962

[43] Koshino M and Ando T 2010 Anomalous orbital magnetism in dirac-electron systems: role of pseudospin paramagnetism Phys. Rev. B 81 195431

[44] Wang Q H, Kalantar-Zadeh K, Kis A, Coleman J N and Strano M S 2012 Electronics and optoelectronics of two-dimensional transition metal dichalcogenides Nat. Nanotechnol. 7 699–712

[45] Zahid F, Liu L, Zhu Y, Wang J and Guo H 2013 A generic tight-binding model for monolayer, bilayer and bulk mos, AJP Adv. 3 052111

[46] Cappelluti E, Roldán R, Silva-Guillén J, Ordejón P and Guinea F 2013 Tight-binding model and direct-gap indirect-gap transition in single-layer and multilayer mos, Phys. Rev. B 88 075409

[47] Rickel E, Le D, Rahman T, Muccioni E and Lewenkopf C 2015 A tight-binding model for mos, monolayers J. Phys.: Condens. Matter 27 365501

[48] Liu G-B, Shan W-Y, Yao Y, Yao W and Xiao D 2013 Three-band tight-binding model for monolayers of group-vib transition metal dichalcogenides Phys. Rev. B 88 085433

[49] Kormányos A, Burkard G, Mitrani F, Sloboda J, Zólyomi V, Drummond N D and Falco V 2015 k·p theory for two-dimensional transition metal dichalcogenide semiconductors 2D Mater. 2 022001

[50] Liu G-B, Xiao D, Yao Y, Xu X and Yao W 2015 Electronic structures and theoretical modelling of two-dimensional group-vib transition metal dichalcogenides Chem. Soc. Rev. 44 2643–63

[51] Tahir M, Vasilopoulos P and Peeters F M 2016 Quantum magnetotransport properties of a mos, monolayer Phys. Rev. B 93 035306

[52] Rose F, Goehring M O and Piccin F 2013 Spin- and valley-dependent magnetoptical properties of mos, Phys. Rev. B 88 125438

[53] Xiao D, Liu G-B, Feng W, Xu X and Yao W 2012 Coupled spin and valley physics in monolayers of mos, and other group-vi dichalcogenides Phys. Rev. Lett. 108 196802

[54] Chu R-L, Li X, Wu S, Niu Q, Yao W, Xu X and Zhang C 2014 Valley-splitting and valley-dependent inter-Landau-level optical transitions in monolayer mos, Quantum Hall systems Phys. Rev. B 90 045427
[55] MacNeill D, Heikes C, Mak K F, Anderson Z, Kormányos A, Zólyomi V, Park J and Ralph D C 2015 Breaking of valley degeneracy by magnetic field in monolayer $\text{mOSe}_2$, Phys. Rev. Lett. 114 037401

[56] Rostami H and Asgari R 2015 Valley Zeeman effect and spin-valley polarized conductance in monolayer $\text{mOSe}_2$ in a perpendicular magnetic field Phys. Rev. B 91 075433

[57] Sakuma R 2013 Symmetry-adapted wannier functions in the maximal localization procedure Phys. Rev. B 87 235109

[58] Gmitra M, Konschuh S, Ertler C, Ambrosch-Draxl C and Fabian J 2009 Band-structure topologies of graphene: spin–orbit coupling effects from first principles Phys. Rev. B 80 235431

[59] Konschuh S, Gmitra M and Fabian J 2010 Tight-binding theory of the spin–orbit coupling in graphene Phys. Rev. B 82 245412

[60] Min H, Hill J E, Sinitisyn N A, Sahu B R, Kleinman L and MacDonald A H 2006 Intrinsic and rashba spin–orbit interactions in graphene sheets Phys. Rev. B 74 165310

[61] Yao Y, Ye F, Qi X-L, Zhang S-C and Fang Z 2007 Spin–orbit gap of graphene: first-principles calculations Phys. Rev. B 75 041401

[62] Thonhauser T, Ceresoli D, Vanderbilt D and Resta R 2005 Orbital magnetization in periodic insulators Phys. Rev. Lett. 95 137205

[63] Resta R 2010 Electrical polarization and orbital magnetization: the modern theories J. Phys.: Condens. Matter 22 123201

[64] Ceresoli D, Thonhauser T, Vanderbilt D and Resta R 2006 Orbital magnetization in crystalline solids: multi-band insulators, chern insulators, and metals Phys. Rev. B 74 024408

[65] Castellanos-Gomez A et al 2014 Isolation and characterization of few-layer black phosphorus 2D Mater. 1 025001

[66] Takao Y and Morita A 1981 Electronic structure of black phosphorus: tight binding approach Physica B+C 105 93–8

[67] Rudenko A N and Katsnelson M I 2014 Quasiparticle band structure and tight-binding model for single-and bilayer black phosphorus Phys. Rev. B 89 201408

[68] Rudenko A, Yuan S and Katsnelson M 2015 Toward a realistic description of multilayer black phosphorus: from g w approximation to large-scale tight-binding simulations Phys. Rev. B 92 085419

[69] Zhou X, Zhang R, Sun J, Zou Y, Zhang D, Lou W, Cheng F, Zhou G, Zhai F and Chang K 2015 Landau levels and magneto-transport property of monolayer phosphorene Sci. Rep. 5 12295

[70] Deckbchi L, Eriksson O and Lebégue S 2015 Two-dimensional indium selenides compounds: an $\alpha$-initio study J. Phys.Chem. Lett. 6 3098–103

[71] Lauth J et al 2016 Solution–processed two-dimensional ultrathin insee nanosheets Chem. Mater. 28 1728–36

[72] Lei S et al 2014 Evolution of the electronic band structure and efficient photo-detection in atomic layers of insee ACS Nano 8 1263–72

[73] Balakrishnan N, Kudrynskyy Z R, Fay M W, Mudd G W, Svatek S A, Makarovsky O, Kovalyuk Z D, Eaves L, Beton P H and Patané A 2014 Room temperature electroluminescence from mechanically formed van der waals iii–vi homojunctions and heterojunctions Adv. Opt. Mater. 2 1064–9

[74] Brotons-Gisbert M et al 2016 Nanotexturing to enhance photoluminescent response of atomically thin indium selenide with highly tunable band gap Nano Lett. 16 3221–9

[75] Kalantar-Zadeh K et al 2010 Synthesis of nanometre-thick $\text{mOSe}_2$ sheets Nanoscale 2 429–33

[76] Molina-Mendoza A J et al 2015 Synthesis of nanometre-thick $\text{mOSe}_2$ sheets arXiv:1512.04355

[77] Goebbels M et al 2014 Measure of diracness in two-dimensional semiconductors Europhys. Lett. 105 57005

[78] Peredew J P, Burke K and Ernzerhof M 1996 Generalized gradient approximation made simple Phys. Rev. Lett. 77 3865–8

[79] Lejaeghere K et al 2016 Reproducibility in density functional theory calculations of solids Science 351 8a3000

[80] Lehoucq R B, Sorensen D C and Yang C 1998 ARPACK Users’ Guide: Solution of Large-Scale Eigenvalue Problems with Implicitly Restarted Arnoldi Methods vol 6 (Philadelphia: SIAM)