Magnetic bulk photovoltaic effect: Strong and weak field

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Magnetic Bulk Photovoltaic Effect: Strong and Weak Field

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Shift current and ballistic current have been proposed to explain the bulk photovoltaic effect (BPVE), and there have been experiments designed to separate the two mechanisms. These experiments are based on the assumption that under magnetic field, ballistic current can have a Hall effect while the shift current cannot, which is from some energy-scale arguments and has never been proven. A recent work [*Phys. Rev. B* **103**, 195203 (2021)] using quantum transport formalism achieves a conclusion that shift current indeed has a Hall current, seemingly contradicting the previous assumption and making the situation more confusing. Moreover, the behavior of BPVE under strong magnetic field is still unexplored. In this Letter, using a minimal 2D tight-binding model, we carry out a systematic numerical study of the BPVE under weak and strong magnetic field by treating the field in a non-perturbative way. Our model clearly shows the appearance of the magnetically-induced ballistic current along the transverse direction, which agrees with the previous predictions, and interestingly a sizable longitudinal response of the shift current is also observed, a phenomenon that is not captured by any existing theories where the magnetic field is treated perturbatively. More surprisingly, drastically different shift current is found in the strong-field regime, and the evolution from weak to strong field resembles a phase transition. We hope that our work could resolve the debate over the behavior of BPVE under magnetic field, and the strong-field behavior of shift current is expected to inspire more studies on the relation between nonlinear optics and quantum geometry.

Keywords: BPVE, shift current, ballistic current, magnetic field, Hall effect

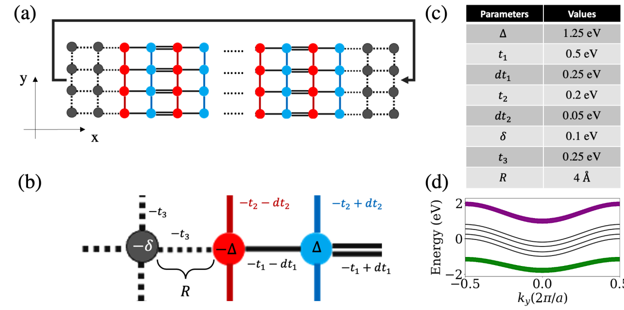
Introduction. The bulk photovoltaic effect (BPVE) refers to the DC current generation from uniform light illumination in a homogeneous material lacking inversion symmetry, in contrast to the traditional photovoltaic effect which requires a heterojunction [1, 2]. To explain this phenomenon, two major different but complementary mechanisms were proposed, namely, *shift current* and *ballistic current* [3]. Ballistic current can be understood as a classical current which originates from the asymmetric momentum distribution of carriers after the light excitation, while shift current is a pure quantum effect and can be attributed to the wave packet evolution during the interband transition [2, 4, 5]. Intuitively, shift current describes the coordinate shift in real-space during the transition [4]. Since these two theories were proposed, there have been experimental attempts to separate and validate them based on the assumption that the ballistic current involves carrier movement and can thus give rise to a Hall current under magnetic field, whereas shift current is barely influenced by any realistic magnetic field [6, 7].

This assumption stems from an early work by Ivechenko *et al.* [8] in which the response of shift current and ballistic current to magnetic field was discussed. Due to the classical nature of ballistic current, a Lorentz force could be exerted on the charge carriers when applying a uniform and static magnetic field, diverting the ballistic current to the transverse direction and thus generating a Hall signal. Built on this idea and considering the electron-phonon coupling as the source of the asymmetric momentum distribution, it is straightforward to set up the Boltzmann transport equation to compute the Hall current of ballistic current. For shift current, however, only a statement without further proof was made about its response to magnetic field, that is, when the cyclotron frequency of the magnetic field is much smaller than the difference between the photon energy and the band gap, the shift current would not be influenced. This statement was solely based on the energy scale of the magnetic field and the electronic system, so it could be misleading, as the magnetic field is known to have an impact on the phase of the wave function (Aharonov-Bohm effect, for example) [9], which is directly related to the shift current that explicitly depends on the phase of the transition momentum matrix [4]. Thus, the previous claim about shift current responsiveness to magnetic field is elusive and remains controversial.

Indeed, Hornung and von Baltz recently revisited this problem by using the quantum transport equation built upon non-equilibrium Green's functions formalism, where they seem to arrive at a conclusion that the shift current can also have a Hall-like response to magnetic field [10]. Specifically, their way of incorporating the magnetic field is to add the induced phase to the Green's function expressed in the position representation, and then expand the phase factor in a Taylor series and retain the zeroth- and linear-order terms. Such treatment will generate a transverse current that is proportional to the non-magnetic shift current, which made those authors conclude that the shift current could have Hall signal. However, a close inspection of their result will reveal that this current is the same as the "magnetically-induced photogalvanic effect" in Ivechenko et al. [8], which is attributed to the breaking of time-reversal symmetry that causes the asymmetry of the momentum distribution (characteristic of ballistic current). Thus, both works achieved the same insight that under magnetic field, a new current along the Hall direction will emerge that is of ballistic type. We will call this new current *magnetically-induced ballistic current* (or mag-BC) in this Letter to distinguish it from electron-phonon or electron-hole ballistic current (which we just call ballistic current) [5, 11] . No further discussion and investigation has been previously made about how shift current itself changes under magnetic field.

One common feature of the previous works is that they both consider the impact of magnetic field as a small perturbation. This could be problematic since even a small magnetic field could have a nontrivial influence on the electronic states; for example, a magnetic field gives rise to the famous fractal band structure known as the Hofstadter butterfly [12]. Hence, one should be cautious when applying the conclusions made in the aforementioned works to experimental design, and it is crucial to examine the magnetic BPVE non-perturbatively so as to understand the applicability of such conclusions. To this end, in this Letter we employ a non-perturbative approach to investigate the behavior of BPVE under weak and strong magnetic field. Our study is carried out in a two-band tight-binding model, but the approach established here can be easily extended to *ab initio* calculations for more realistic systems with the help of Wannierization [13–15]. The numerical results from our simulation clearly show the existence of transverse mag-BC under weak field, but more surprisingly, the shift current will also have an appreciable longitudinal response to weak field. Moreover, the strong magnetic field will drastically change the shift current spectrum so that two electronic phases in terms of the BPVE can be identified. To the best of our knowledge, this is the first systematic numerical study on magnetic BPVE.

Model. The simplest tight-binding model that breaks the inversion symmetry is the 1D Rice-Mele model (along x-direction, longitudinal) which has alternating onsite energies and hoppings [16, 17]. To study the Hall effect in a non-centrosymmetric system, we create a 2D tight-binding model by periodically repeating the long but finite Rice-Mele chain along the second dimension (y-direction, transverse) and adding a staggered hopping that connects them. In order to model the short-circuit condition, two leads are attached to the ends of the Rice-Mele chain, and hopping from one lead to the other is allowed [18]. All the bond lengths are chosen to be the same to simplify the model. The model can be seen in Fig 1a [the corresponding Hamiltonian can be found in the Supplementary Material [19] (see also references [4, 20, 21] therein)], and the parameters and the chosen values for them in this work can be seen in Fig 1(b) and (c). In



Parameters	Values
Δ	1.25 eV
t_1	0.5 eV
dt_1	0.25 eV
t_2	0.2 eV
dt_2	0.05 eV
δ	0.1 eV
t_3	0.25 eV
R	4 Å

FIG. 1. The model used in this work and the chosen parameters. (a) The 2D tight-binding model used for calculating the magnetic BPVE. Blue and red atoms represent the optically active region while the gray atoms represent the leads. The short-circuit condition is imposed by allowing hopping between the two leads. (b) The parameters involved in the tight-binding model. (c) The values chosen for the parameters. (d) The band structure for non-magnetic system. The bands in black correspond to leads and are not included when computing BPVE. The Fermi energy is chosen at 0 eV so that there is no partial occupation in valence bands and conduction bands.

this work, there are 400 sites in the central region and 4 sites in the leads. Adding more atoms in the leads does not change the results [19].

To investigate the magnetic BPVE, we consider a static and uniform magnetic field perpendicular to the 2D system and focused on the optically active central region (extending the magnetic field to the leads will have no impact [19].). The influence of the magnetic field on the electronic structure can be incorporated via the so-called Peierls substitution [12, 22, 23], $t_{ij} \rightarrow t_{ij} \exp\left(i\frac{e}{\hbar}\int_{\boldsymbol{R_i}}^{\boldsymbol{R_j}} \boldsymbol{A}_B \cdot d\boldsymbol{r}\right)$, where $\boldsymbol{A}_B$ is the vector potential of the magnetic field and t_{ij} denotes the general hopping from lattice site i to site j, and the integral follows the straight line from i to j. The Peierls substitution can be justified by doing the $\mathbf{p} \rightarrow \mathbf{p} - q\mathbf{A}_B$ replacement in the Hamiltonian and modifying the atomic orbitals by multiplying an extra phase $\frac{e}{\hbar}\int_{\boldsymbol{R}}^{\boldsymbol{r}} \boldsymbol{A}_B \cdot d\boldsymbol{r}$ when deriving the tight-binding Hamiltonian. If we use the Landau gauge $\boldsymbol{A}_B = (0, Bx, 0)$, then for our system the Peierls phase will be $\frac{eB}{\hbar}\frac{(R_{j,y}-R_{i,y})(R_{j,x}+R_{i,x})}{2}$. In this way, the influence of the magnetic field has been treated non-perturbatively. As the expression of shift current is invariant under the magnetic field (see [19] and [21]), the shift current response can be calculated according to the formula[4]:

$$j_{rsq}^{sh} = \frac{\pi e^3}{\hbar\omega^2}\sum_{n,l}\sum_{r,s}\int_{BZ}\frac{d\boldsymbol{k}}{(2\pi)^3}\left(f_{l\boldsymbol{k}} - f_{n\boldsymbol{k}}\right)v_{nl}^s(\boldsymbol{k})v_{ln}^r(\boldsymbol{k}) \times\left[-\frac{\partial\phi_{nl}^r(\boldsymbol{k})}{\partial k_q} - \left[\chi_{lq}(\boldsymbol{k}) - \chi_{nq}(\boldsymbol{k})\right]\right]\delta\left(\varepsilon_{l\boldsymbol{k}} - \varepsilon_{n\boldsymbol{k}} \pm \hbar\omega\right). \tag{1}$$

Here, $\chi_{nq}(\boldsymbol{k}) \equiv \langle u_{n\boldsymbol{k}} | i\partial_{k_q} u_{n\boldsymbol{k}} \rangle$ is Berry connection, and $\phi^r_{nl}(\boldsymbol{k})$ is the phase of the velocity matrix $v^r_{nl}(\boldsymbol{k}) \equiv \langle n\boldsymbol{k}|\hat{v}^r|l\boldsymbol{k}\rangle$. In addition to the shift current which comes from the off-diagonal elements of the density matrix, the diagonal part of the density matrix will also have a non-vanishing contribution, unlike the more well-studied situation where there exists time-reversal symmetry that causes the diagonal contribution to be exactly zero. The newly emergent contribution from the diagonal part of the density matrix (asymmetric momentum distribution), as alluded above, is termed as mag-BC and can be calculated from the following formula [24, 25]:

$$j^{mag-BC}_{rsq} = \frac{\pi e^3 \tau}{\hbar\omega^2} \mathrm{Re}\Bigg[\sum_{l,n}\sum_{r,s}\int_{BZ}\frac{d\boldsymbol{k}}{(2\pi)^3}(f_{l\boldsymbol{k}} - f_{n\boldsymbol{k}}) \times v^r_{nl}(\boldsymbol{k}) v^s_{ln}(\boldsymbol{k}) v^q_{nn}(\boldsymbol{k}) \delta(\varepsilon_{n\boldsymbol{k}} - \varepsilon_{l\boldsymbol{k}} \pm \hbar\omega)\Bigg]. \quad (2)$$

We choose $\tau = 100$ fs in all of the calculations. As we are interested in the BPVE from the central region, we manually exclude the contributions from the bands of the leads when performing the summation of bands in Eqs. (1) and (2). Moreover, we will restrict our discussion to the linear light-polarization along the x- (longitudinal) direction, and we only show the longitudinal (xxX) shift current and transverse (xxY) mag-BC as the system symmetry enforces that the other components will be zero [19]. A test of our model is presented in Supplementary Material [19], which shows excellent agreement of shift current and mag-BC obtained from a bulk system and from our model with leads, for both non-magnetic case and commensurate magnetic field (i.e., when the magnetic flux through the central region is equal to an integer number of flux quanta h/e). After showing the validity of our model, we use this model to explore in more detail how BPVE behaves at weak and strong magnetic field.

Weak magnetic field. Experimentally, a relatively weak magnetic field below 0.5 T is easily accessible, and it is in this regime where most of the controversy over the magnetic field influence on shift current occurs. So, it would be of interest to show the response of BPVE to a weak field. Shown in Fig. 2a is the xxY mag-BC for magnetic field from -0.5 T to 0.5 T. When $B = 0$ T, the mag-BC vanishes due to the existence of time-reversal symmetry, but once the magnetic field is turned on, mag-BC appears and scales linearly with the B field strength, as can be seen in Fig. 2b. This is in agreement with the previous publications [8, 10] which also predicted a linear scaling of mag-BC $j^{mag-BC}_{\perp} = xBj^{sh}_{\parallel}$, where $j^{sh}_{\parallel}$ is the non-magnetic longitudinal shift current while $j^{mag-BC}_{\perp}$ is the mag-BC along the transverse direction. (Though a close comparison between Fig. S1 [19] and Fig. 2a reveals that the scaling coefficient x is weakly frequency-dependent.) Thus, in a sense mag-BC can be taken as a transverse response of shift current under the magnetic field, but it is not appropriate to interpret it as a classical Hall effect as will be discussed later.

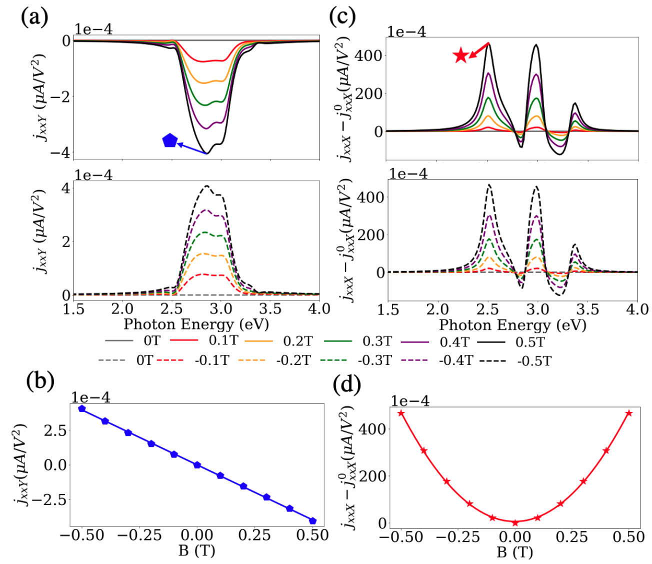


FIG. 2. Magnetic BPVE in the weak-field regime. (a) The response of the xxY mag-BC with weak magnetic field. (b) The scaling of mag-BC is linear in this regime for the selected peak (labeled by the blue pentagon in (a)). The existence and the scaling of mag-BC is consistent with the previous predictions [8, 10], but its magnitude is very small and even smaller than the response of the shift current shown in (d). (c) The response of the xxX shift current with weak magnetic field. Different from previous predictions by [8, 10], the shift current will respond to magnetic field quadratically, as can be seen from (d) for the selected peak (labeled by red star in (c)), even when the corresponding cyclotron frequency is much lower than the difference between photon energy and band gap.

To make connections with experiments [6, 7] where a weak magnetic field was used to separate the shift current and ballistic current, it is worth noting that the mag-BC (Fig. 2b) is five orders smaller than the non-magnetic shift current (Fig. S1a and S1b [19]), in contrast to the Hall effect of ballistic current which is only two orders smaller [6–8]. In other words, the scaling coefficient x should be much smaller than 1. Therefore, one can safely neglect the contribution from mag-BC when analyzing the transverse current found in experiments with weak magnetic fields.

What is not captured by existing theories is that there is also a finite response of shift current to magnetic field (Fig. 2c and 2d), which is even larger than mag-BC (Fig. 2b. The response is symmetric with respect to positive and negative magnetic field, so it can only be described by even orders of response. Such nonlinear behavior is reminiscent of the longitudinal current in classical Drude model for Hall effect, but unlike the Drude model, some peaks of the shift current will increase in-

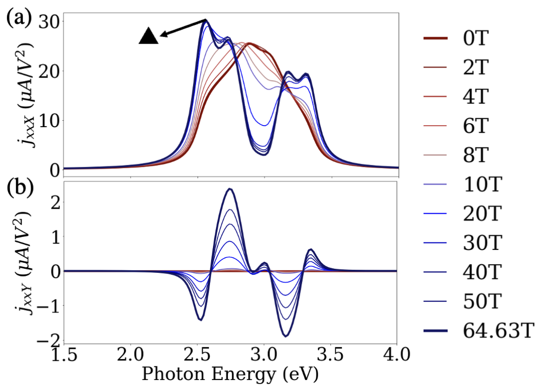


FIG. 3. The transition of the magnetic BPVE from weak field to strong field. (a) The evolution of xxX shift current. Below 8 T, the profile is relatively constant but continues to grow quadratically. Above 20 T, the profile is also relative constant, though the lineshape is significantly different. Between 8 T and 20 T there is an intermediate regime where the low-field profile will transition into the strong-field profile. The evolution of the peak labeled by the black triangle is plotted in Fig. 4a. (b) The evolution of xxY mag-BC. Unlike the shift current, the mag-BC does not stabilize into two phases but continues to grow as the magnetic field becomes larger (providing stronger time-reversal symmetry breaking).

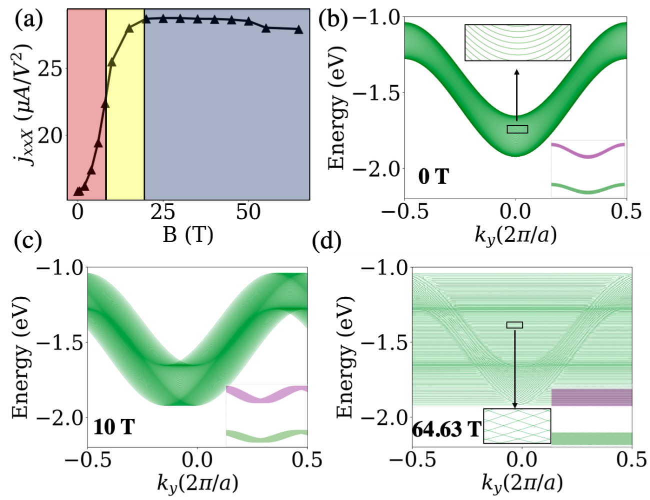


FIG. 4. Evolution of the band structure with magnetic field. (a) The scaling of the shift current response represented by the black triangle in Fig. 3a with magnetic field. (b) The valence bands for the non-magnetic system. (c) The valence bands with 10 T magnetic field. (d) The valence bands under the commensurate magnetic field (64.63 T). For (b)-(d), the insets show both the valence band (green) and conduction band (purple) manifold, and the bands corresponding to leads have been removed.

stead of decrease when the magnetic field is applied [23]. This could be rationalized by the fact that the magnetic field will couple states that are otherwise uncoupled (non-magnetic eigenstates having different crystal momenta, for example). Thus, the longitudinal response of shift current to magnetic field is a distinct quantum effect and cannot be interpreted by classical models, and the failure to predict this response in [8, 10] again shows that the energy-scale argument is not sufficient to explain responses related to the quantum geometry. Moreover, the increasing magnitude of the longitudinal shift current also makes the interpretation of mag-BC as the classical Hall effect of shift current[10], i.e. the diversion of shift current to the transverse direction, questionable since the diversion would make the shift current smaller. As a result, it is more appropriate to interpret mag-BC as a new type of ballistic current originating from the asymmetric scattering due to the magnetic field.

Strong magnetic field. Comparing the non-magnetic shift current with the same quantity under the commensurate magnetic field (64.63 T) in Fig. S1a [19], raises the question of how the spectrum evolves with increasing B field, since it appears that the weak-field response shown in Fig. 2c will not lead simply to the strong-field response. Thus, we further increase the magnetic field gradually to 64.64 T and observe the change of the shift current lineshape. (A preliminary exploration of the shift current response beyond 64.63 T can be found in Supplementary Material [19].) The numerical results indicate that the shift current experiences a phase-transition-like change as shown in Figs. 3a and 4a. Below 8 T, the lineshape of shift current is relatively constant despite the sizable quadratic response shown in Fig. 2c, while between 8 T and 20 T, the shift current experiences rapid changes so that its lineshape begins to show the essential features of the strong-field response. Above 20 T, however, the lineshape again remains relative constant and exhibits a weak dependence on the magnetic field.

To our knowledge, such peculiarity in the magnetic-field-induced change in BPVE has not been previously reported. Since magnetic field affects the wave-vector-dependent wave function phases, these findings could be viewed as an example of how nonlinear optics can be used to probe the quantum geometry [26–28]. This can be corroborated by the behavior of the xx component of the absorption coefficient, which does not depend on the phase of the wave functions and thus shows negligible change as magnetic field varies [19]. More concretely, it is the rapid change of band character that is responsible for the evolution of shift current lineshape [29]. In the weak-field regime, all bands are well-separated from each other (Fig. 4b), so that the bands have distinct band character; that is, each band can be largely ascribed to the delocalized states along x- and y- directions as in Fig. 1. As the magnetic field increases and exceeds a certain threshold, the well-separated bands start to mix and cross at some regions of the Brillouin zone (Fig. 4c). Such band crossing is accompanied by a rapid change of the band character, which manifests as the fast change of the shift current lineshape, because the shift vector in

Eq. (1) depends sensitively on band characters [29]. Entering into the strong-field regime, the band structure has a drastically different profile and band crossings happen almost everywhere in the Brillouin zone (Fig. 4c). The band characters are thus totally changed compared with the non-magnetic bands, and therefore the shift current exhibits a completely different lineshape from the non-magnetic counterpart.

Contrary to the shift current, mag-BC is related to the asymmetry of the carrier generation rate, which is a result of the breaking of time-reversal symmetry caused by magnetic field. So the mag-BC is more well-behaved in the sense that it will appear and become larger for stronger magnetic field (Fig. 3b), as a stronger field strength would break the time-reversal-symmetry to a larger extent. On the other hand, mag-BC can also feel the evolution of the band structure (Fig. 4b and Fig. S5) so that the peaks between 2.55–3.2 eV will shift their position somewhat, and so the trends of the magnitudes at any one photon energy are not monotonic. Nonetheless, the mag-BC will not stabilize into a constant lineshape as the shift current does and is always responsive to magnetic field.

Summary. In this Letter, we report a systematic numerical study of the bulk photovoltaic effect under both weak and strong magnetic field. Our results clearly demonstrate the existence of transverse magnetically-induced ballistic current as predicted by several previous works, and a sizable longitudinal response from shift current to magnetic field is also revealed. Moreover, an interesting and surprising behavior for shift current when going from weak-field to strong-field is discovered, showing a phase-transition-like change in the lineshape. We expect that this finding will inspire more studies on the relations between quantum geometry and nonlinear optics.

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[1] V. I. Belinicher and B. I. Sturman, Sov. Phys. USP. **23**, 199 (1980).
[2] R. von Baltz and W. Kraut, Phys. Rev. B **23**, 5590 (1981).
[3] V. I. Belinicher, Ferroelectrics **83**, 29 (1988).
[4] S. M. Young and A. M. Rappe, Phys. Rev. Lett. **109**, 116601 (2012).
[5] Z. Dai, A. M. Schankler, L. Gao, L. Z. Tan, and A. M. Rappe, Physical Review Letters **126**, 177403 (2021).
[6] A. M. Burger, R. Agarwal, A. Aprelev, E. Schruba, A. Gutierrez-Perez, V. M. Fridkin, and J. E. Spanier, Science advances **5**, eaau5588 (2019).
[7] A. M. Burger, L. Gao, R. Agarwal, A. Aprelev, J. E. Spanier, A. M. Rappe, and V. M. Fridkin, Physical Review B **102**, 081113 (2020).
[8] E. L. Ivchenko, Y. B. Lyandageller, G. E. Pikus, and R. Y. Rasulov, Soviet Physics Semiconductors-USSR **18**, 55 (1984).
[9] D. J. Thouless, M. Kohmoto, M. P. Nightingale, and M. den Nijs, Physical Review Letters **49**, 405 (1982).
[10] D. Hornung and R. von Baltz, Physical Review B **103**, 195203 (2021).
[11] Z. Dai and A. M. Rappe, Physical Review B **104**, 235203 (2021).
[12] D. R. Hofstadter, Physical review B **14**, 2239 (1976).
[13] N. Marzari, A. A. Mostofi, J. R. Yates, I. Souza, and D. Vanderbilt, Reviews of Modern Physics **84**, 1419 (2012).
[14] G. Pizzi, V. Vitale, R. Arita, S. Blügel, F. Freimuth, G. Géranton, M. Gibertini, D. Gresch, C. Johnson, T. Koretsune, J. Ibañez-Azpiroz, H. Lee, J.-M. Lihm, D. Marchand, A. Marrazzo, Y. Mokrousov, J. I. Mustafa, Y. Nohara, Y. Nomura, L. Paulatto, S. Poncé, T. Ponweiser, J. Qiao, F. Thöle, S. S. Tsirkin, M. Wierzbowska, N. Marzari, D. Vanderbilt, I. Souza, A. A. Mostofi, and J. R. Yates, Journal of Physics: Condensed Matter **32**, 165902 (2020).
[15] J. Lado and J. Fernández-Rossier, 2D Materials **3**, 035023 (2016).
[16] M. Rice and E. Mele, Physical Review Letters **49**, 1455 (1982).
[17] H. Ishizuka and N. Nagaosa, New Journal of Physics **19**, 033015 (2017).
[18] A. M. Kolpak, N. Sai, and A. M. Rappe, Phys. Rev. B **74**, 054112 (2006).
[19] See Supplemental Material at [URL will be inserted by publisher] for the exact form of the model Hamiltonian, discussion on the shift current expression under the influence of magnetic field, symmetry analysis, evolution of band structures and mag-BC, discussion on magnetic BPVE for magnetic field beyond the strong-field regime, and benchmarks, which includes Refs. [4, 20, 21].
[20] T. G. Pedersen, K. Pedersen, and T. B. Kriestensen, Physical Review B **63**, 201101 (2001).
[21] L. Gao, Z. Addison, E. Mele, and A. M. Rappe, Physical Review Research **3**, L042032 (2021).
[22] R. Peierls, Zeitschrift für Physik **80**, 763 (1933).
[23] E. Fradkin, *Field theories of condensed matter physics* (Cambridge University Press, 2013).
[24] Y. Zhang, T. Holder, H. Ishizuka, F. de Juan, N. Nagaosa, C. Felser, and B. Yan, Nature Communications **10**, 3783 (2019).
[25] W. Kraut and R. von Baltz, Phys. Rev. B **19**, 1548 (1979).
[26] T. Morimoto and N. Nagaosa, Science Advances **2**, e1501524 (2016).
[27] T. Holder, D. Kaplan, and B. Yan, Physical Review Research **2**, 033100 (2020).
[28] J. Ahn, G.-Y. Guo, N. Nagaosa, and A. Vishwanath, Nature Physics **18**, 290 (2022).
[29] L. Z. Tan and A. M. Rappe, Physical Review Letters **116**, 237402 (2016).