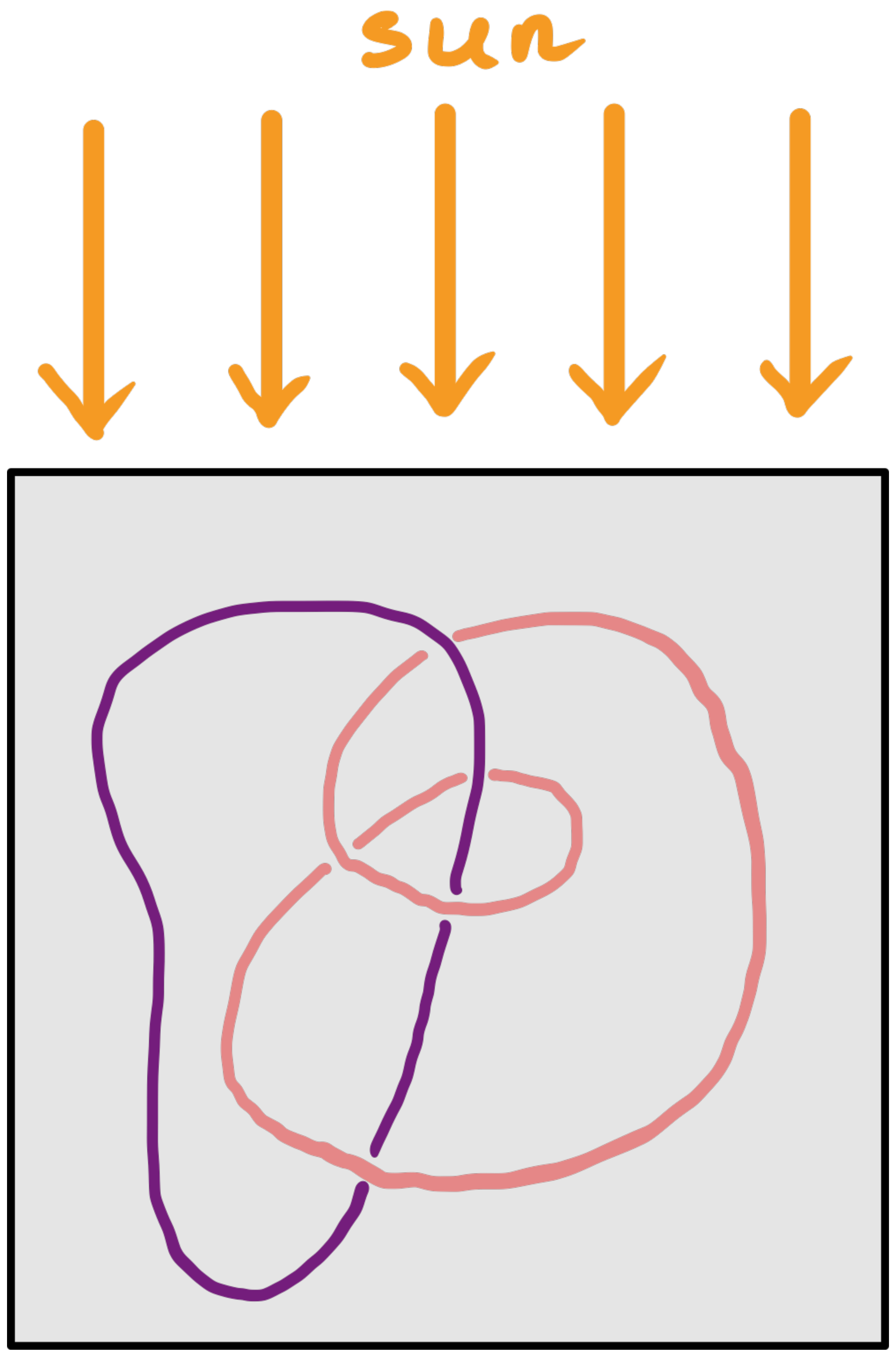
A topological principle in photovoltaics



Aris Alexandradinata

Outline

Review: "Shift' component of photovoltaic current

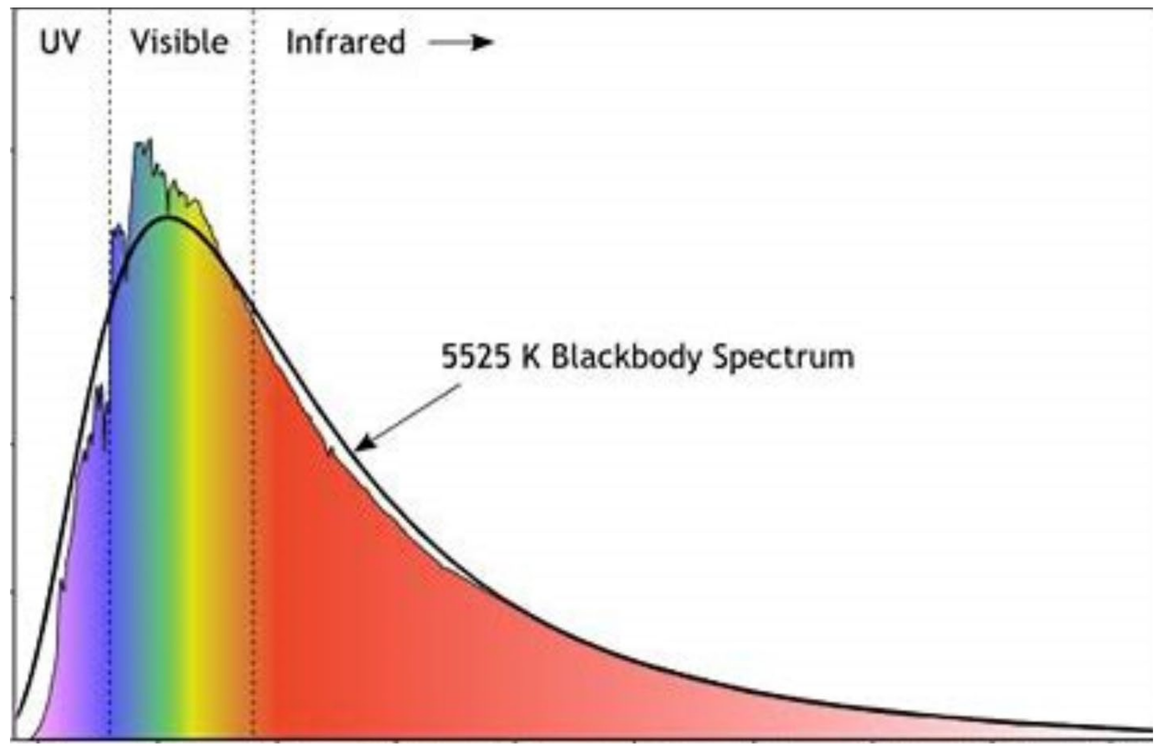
Shift vector ↔ intra- and interband Berry connection

My contribution: First-known class of wide-band-gap TI's with a large shift current

Baby step toward a topological solar cell

Previous works: Topological semimetals/TI with small band gap

⇒ band gap zero/small ⇒ shift current large at low frequency



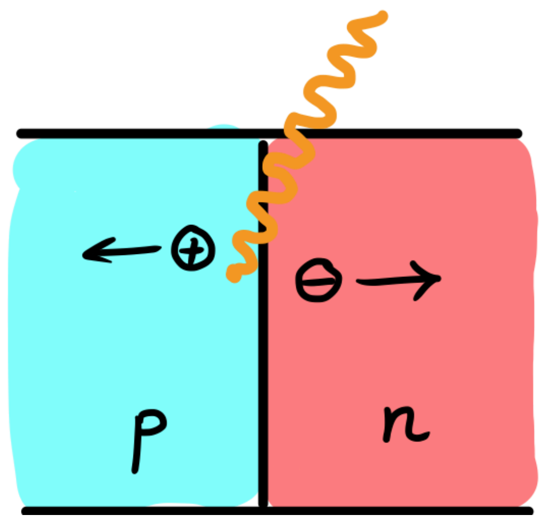
Phenomenological theory of direct photocurrent

(Kraut, Baltz, 1978)

Inhomogeneous medium

$$j_{dc} = \underbrace{j_{drift} + j_{diffusion}} + j_{(2)}$$

Generalized Ohm's law



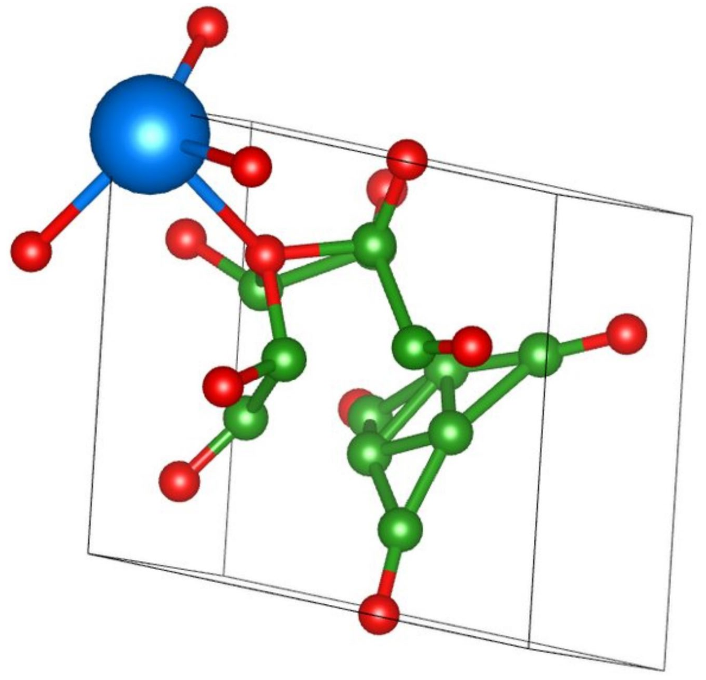
Silicon

Proportional to light intensity

$$j^a_{(2)} = \sigma^{abc}_{(2)}(\omega)E^b(\omega)E^c(-\omega)$$

$\sigma^{abc}_{(2)} = 0$ unless medium breaks centrosymmetry

Goal: maximize $j_{dc} = j_{(2)}$ for homogeneous noncentric crystals

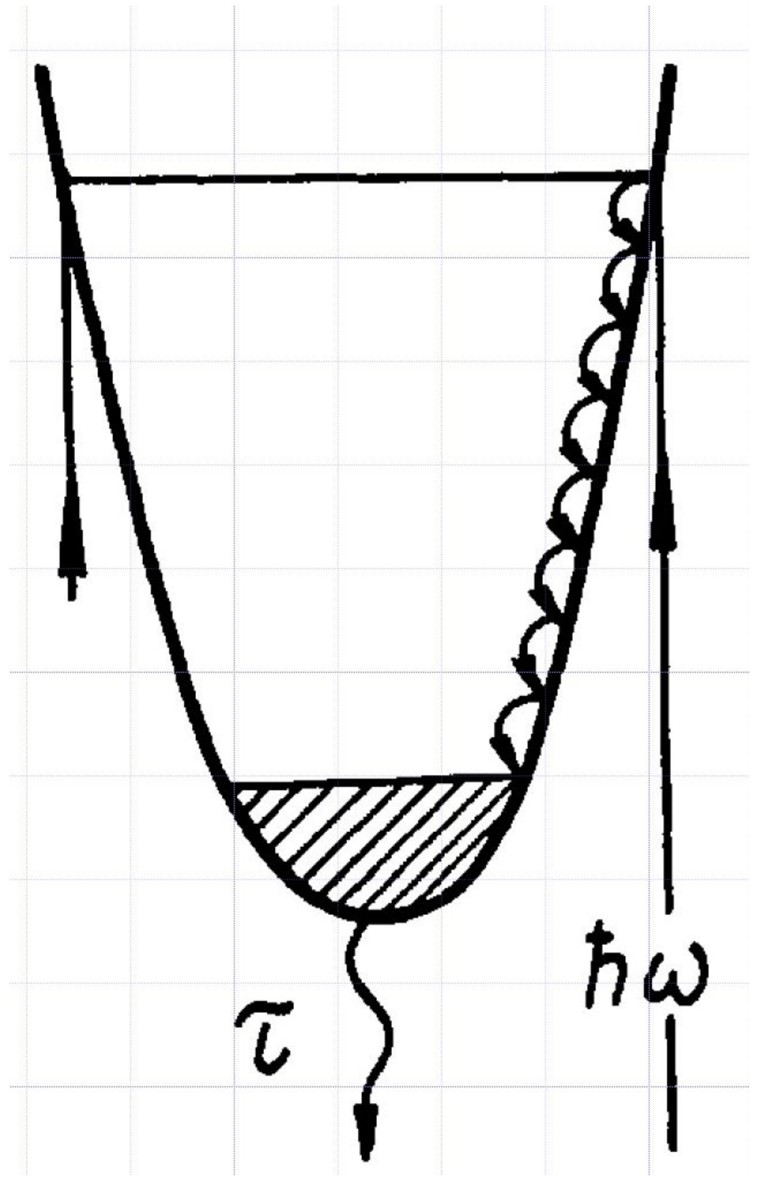


Shift component of second-order photocurrent

$$j_{(2)} = j_{shift} + j_{ballistic}$$

Shift/displacement of quasiparticle wavepacket as it transits between Bloch states

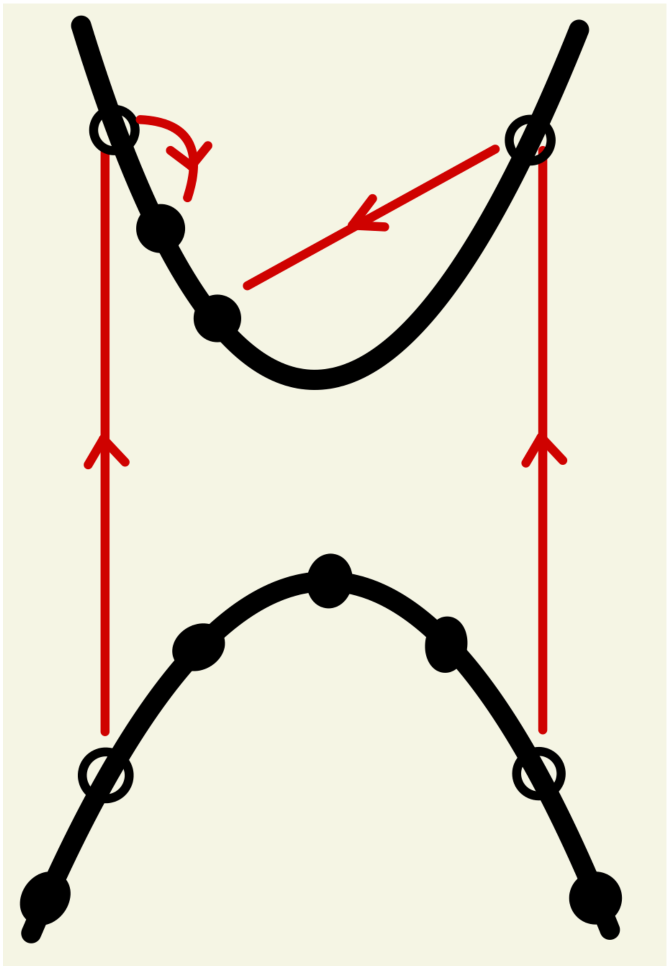
$$(m, \boldsymbol{k}) \rightarrow (n, \boldsymbol{k}')$$



$$j_{shift} \neq 0 \text{ even if } f(k) = f(-k)$$

Current due to ballistic motion of quasiparticles

$$j_{ballistic} \doteq \int v(k)[f(k) - f(-k)]dk$$



$$j_{ballistic} \neq 0 \text{ only if } f(k) \neq f(-k)$$

(Sturman, Fridkin, The photovoltaic and photorefractive effects in noncentrosymmetric materials, 1992)

Modest goal: maximize j_{shift} for homogeneous, noncentric crystals

$$j_{shift} = \frac{e}{Vol}\frac{1}{2}\sum_{m,k}\sum_{n,k'} S_{nk',mk}\left(\frac{dP_{nk'\leftarrow mk}}{dt} - \frac{dP_{mk\leftarrow nk'}}{dt}\right)$$

sum over Bloch-to-Bloch transitions

Shift vector

Forward transition rate

Backward transition rate

Focus first on light-induced shifts

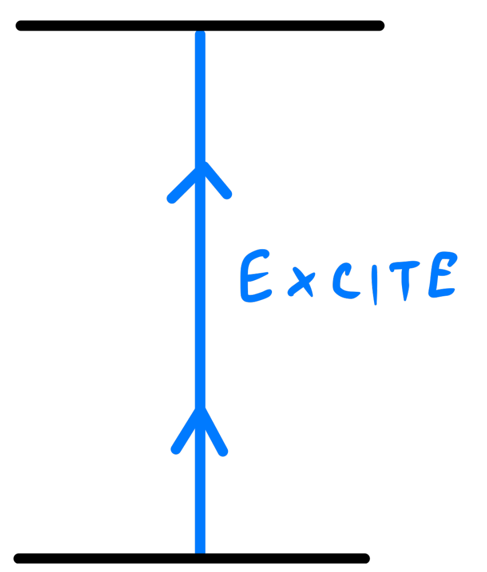
$\lambda \gg a$, neglect photon momentum in vertical transitions: $(m, \boldsymbol{k}) \rightarrow (n, \boldsymbol{k})$

$S_{nm}(\boldsymbol{k})$ depends on **intra**- and **inter**band Berry connection of electronic wave function

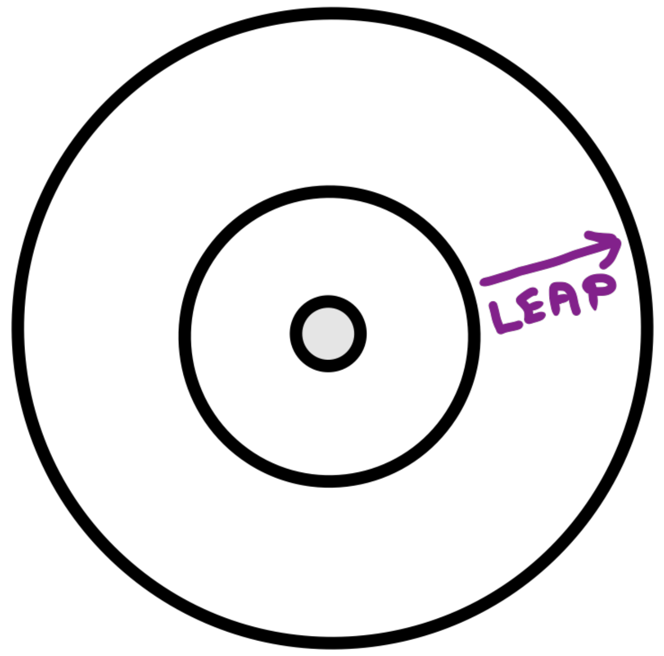
Intraband-Berry component of shift current

Heisenberg's quantum leap

"teleportation":
no intermediate trajectory



Atomic energy levels



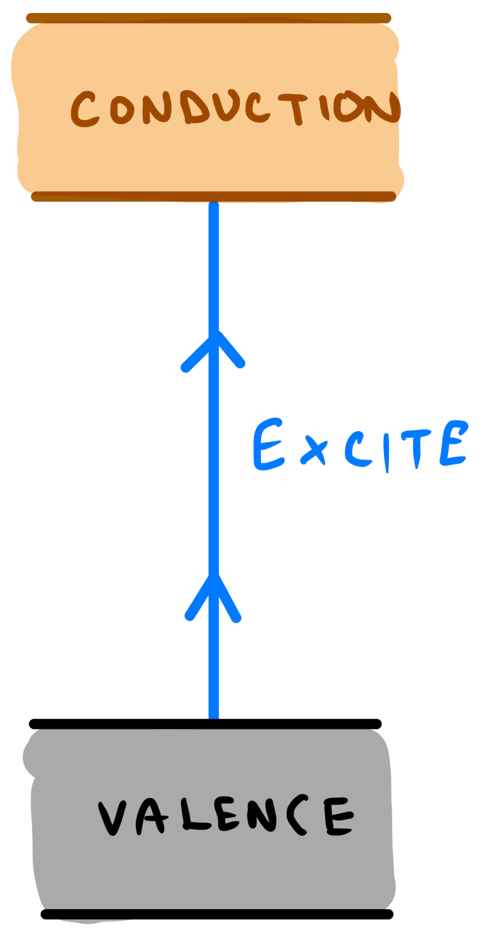
Bohr orbits

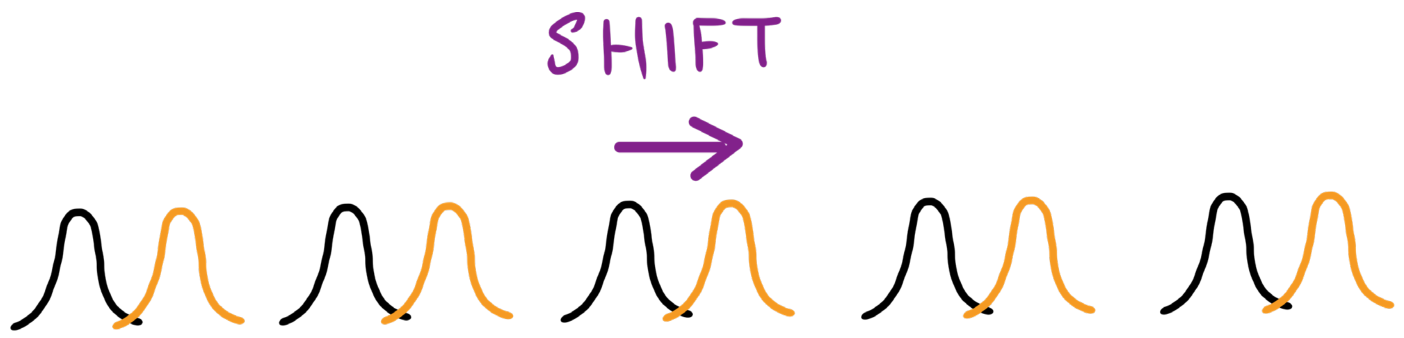
Shift current

$$\text{Bloch state } e^{ikr}u_{mk} \overset{F.T}{\longleftrightarrow} \text{ Wannier orbital}$$

$$i\partial_k \leftrightarrow position$$

$$\frac{\phi_{Berry}}{2\pi} = \int A_m(k)\frac{dk}{2\pi} = \langle position\rangle_{Wannier} \quad \text{(Zak, 1989)}$$





Wannier orbitals

$A_m(k) = \langle u_m | i\nabla_k u_m\rangle$ intraband Berry connection

Suggestive: $S_{nm}(\boldsymbol{k}) = A_n(\boldsymbol{k}) - A_m(\boldsymbol{k})$

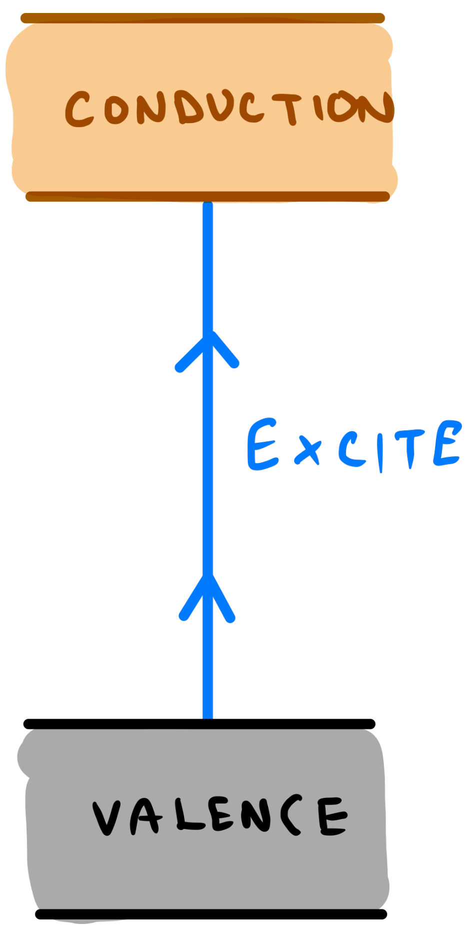
Shift should depend on the light polarization vector $\vec{\boldsymbol{e}}$

Interband-Berry component of shift vector

(Wave packet interpretation by Belinicher, Sturman, 1982)

Wave packet: $|W_n\rangle = \int dk f_{n,k} |n,k\rangle$

$$\langle W_n | r | W_n \rangle = -\nabla_k phase f_{n,k} + A_n(k) + v_n(k)t$$



$$f_{c,k} \doteq \vec{e} \cdot \langle c,k|\vec{r}|v,k\rangle \doteq \vec{e} \cdot \vec{A}_{cv}(k)$$

polarization-dependent dipole matrix element

$A_{cv}(k) = \langle u_c | i\nabla_k u_v \rangle$ **inter**band Berry connection

$$S_{cv}(\boldsymbol{k}) = A_c(\boldsymbol{k}) - A_v(\boldsymbol{k}) - \nabla_k phase[\vec{e} \cdot \vec{A}_{cv}]$$

Only gauge-invariant when combined

$$S_{cv}(\boldsymbol{k}) = A_c(\boldsymbol{k}) - A_v(\boldsymbol{k}) - \nabla_k phase[\vec{e} \cdot \vec{A}_{cv}]$$

Topological materials ↔ large intraband Berry phase

Suggestive: j_{shift} large for topo. materials

Past work

no topological invariant associated to the shift current

Reason: able to tune H to be centrosymmetric while remaining in same topo. phase

Wave function topology is *not* a sufficient condition for a nontrivial shift.

Need supplemental conditions on ***energy*** dispersion:

For Z2 TI: small band gap (Tan, Rappe, 2016)

For TSM: tilting/warping of Dirac cone (Chan, Lindner, Refael, Lee, 2017; Kim, Morimoto, Nagaosa, 2017; Yang, Burch, Ran, 2018; Ahn, Guo, Nagaosa, 2020)

Goal: find a class of TI's for which
wave function topology (by itself) $\Rightarrow$ nontrivial shift

Necessary condition:
being topologically nontrivial is only possible in noncentric space group

intrinsically noncentric TI

(rules out Chern, Kane-Mele, TCI SnTe, KHgSb)

Two propositions for intrinsically noncentric TI:

(P1) $\exists$ invariant Obs[wave function]$\in \mathbb{Z}$
such that $Obs \neq 0 \Rightarrow$ impossible to tune $S(k) = 0$ for all k

Shift obstruction

(P2) wide band gaps + large **transient** j_{shift} under broad-band radiation

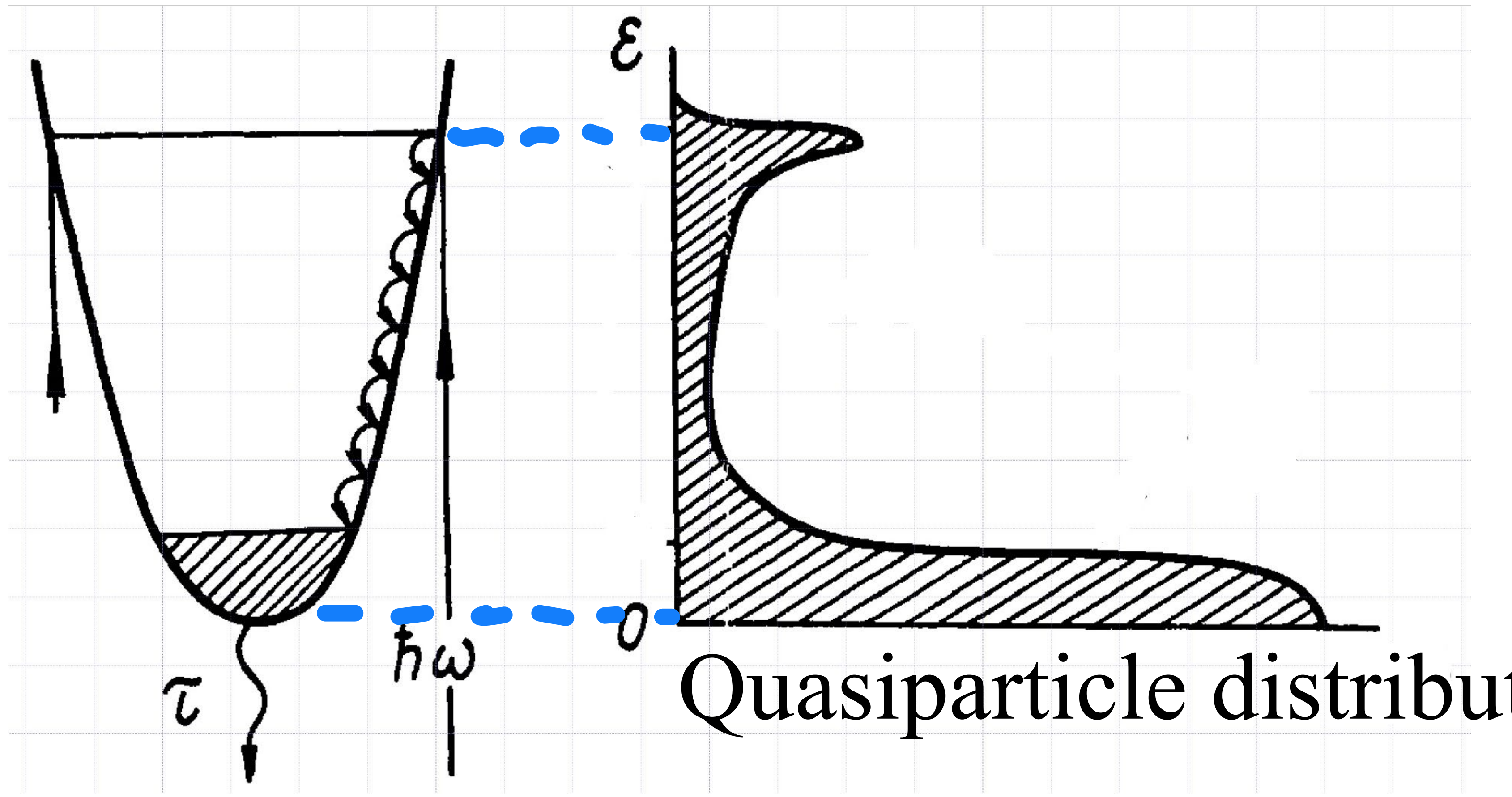
Steady-state vs transient shift current

$$j_{shift} \doteq \sum_{m,k}\sum_{n,k'} S_{nk',mk}\left(\frac{dP_{nk'\leftarrow mk}}{dt} - \frac{dP_{mk\leftarrow nk'}}{dt}\right)$$

Steady state

dP/dt determined by kinetic model

(Belinicher, Sturman, 1982)



Quasiparticle distribution

Only the steady current matters to solar cell applications

Transient (t < relax. time)

Diagonal[density] = $\rho_{T=0;light=0}$

Off-diagonal elements by Kubo-type perturbation theory. (Kraut, Baltz, 1979; Sipe, Shrkrebtii, 2000)

Possibly measurable in ultrafast expt with sub-ps resolution

(P2) wide band gaps + large **transient** j_{shift} under broad-band radiation

need a figure of merit

Monochromatic: $j^a_{shift} = \sigma^{abc}_{Kubo}(\omega) E^b(\omega) E^c(-\omega)$

Broad-band: $\int_{band\ width} \sigma^{abc}_{Kubo} d\omega = F^{abc} \frac{e^3}{h^2}$

dimless figure of merit

<u>Prototypical ferroelectric</u>

BaTiO3: $F \approx 0.01$ (Tan, Rappe, 2012)

PbTiO3: peak[σ_{Kubo}]$\approx 0.05 mAV^{-2}$

<u>Intrinsically noncentric TI</u>

Model H: $F \approx 10\mathbb{Z}$

ave[σ_{Kubo}]$\approx 0.1 mAV^{-2} \times \mathbb{Z}$

Outline for rest of talk

Two propositions for intrinsically noncentric TI:

(P1) Shift obstruction

(P2) Wide band gaps + large **transient** j_{shift}

$(F \approx 10\mathbb{Z})$

Minimal model: 2D, 2-band, reflection-symmetric (or 3D model by stacking)

Generalizations of intrinsically noncentric TI for photovoltaic applications.

Shift obstruction

(P1) $\exists$ invariant Obs[wave function]$\in \mathbb{Z}$

such that $Obs \neq 0 \Rightarrow$ impossible to tune $S(k) = 0$ for all k

$$Obs = -2RTP_v - Vor$$

Intraband Berry (RTP_v)

Interband Berry (Vor)

Intraband component of obstruction invariant

What **intra**band invariant 'maximally' breaks centrosymmetry (*P*) ?

Berry curvature field strength = pseudovector

$P: \vec{\Omega}(k) = \vec{\Omega}(-k)$

→ maximally break centrosymmery

$\vec{\Omega}(k) = -\vec{\Omega}(-k)$

Compatible with time-reversal symmetry

P and *T*: $k \to -k$

P unitary; *T* antiunitary

Want $\int_{BZ/2} \Omega d^2 k$ to be large, quantized in *half* the BZ

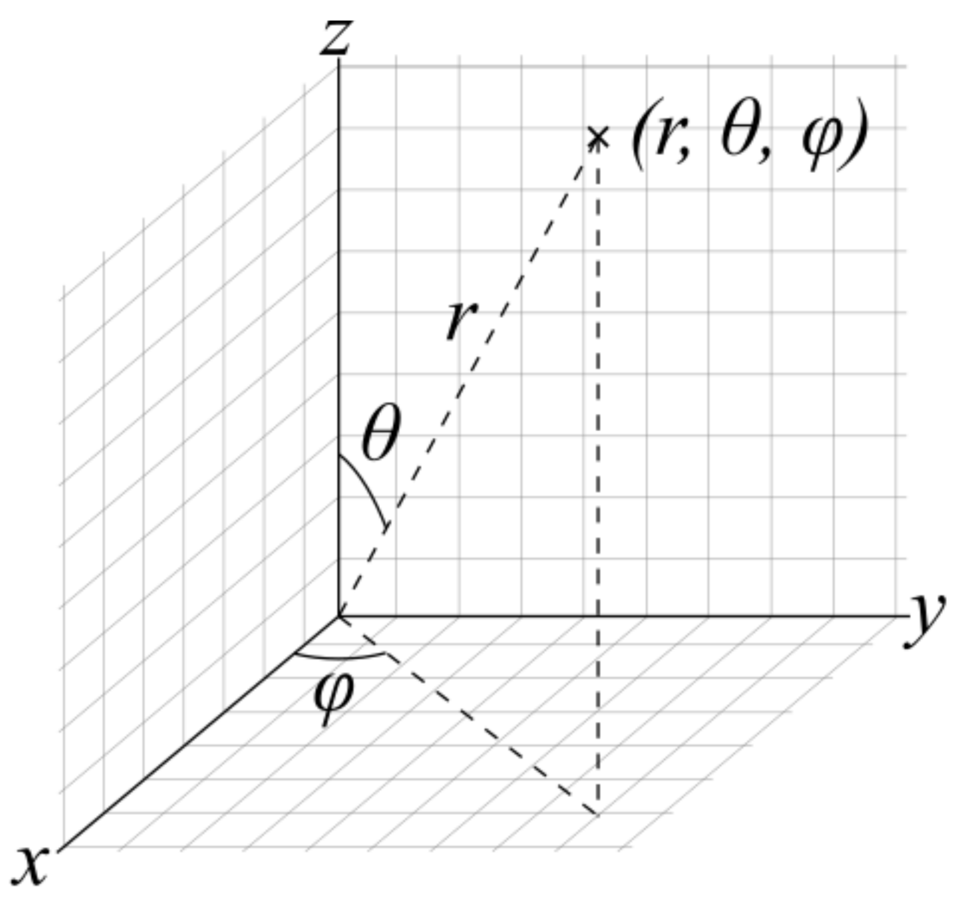
Flatband model of intrinsically noncentric TI

$$H = \vec{d} \cdot \vec{\sigma}$$

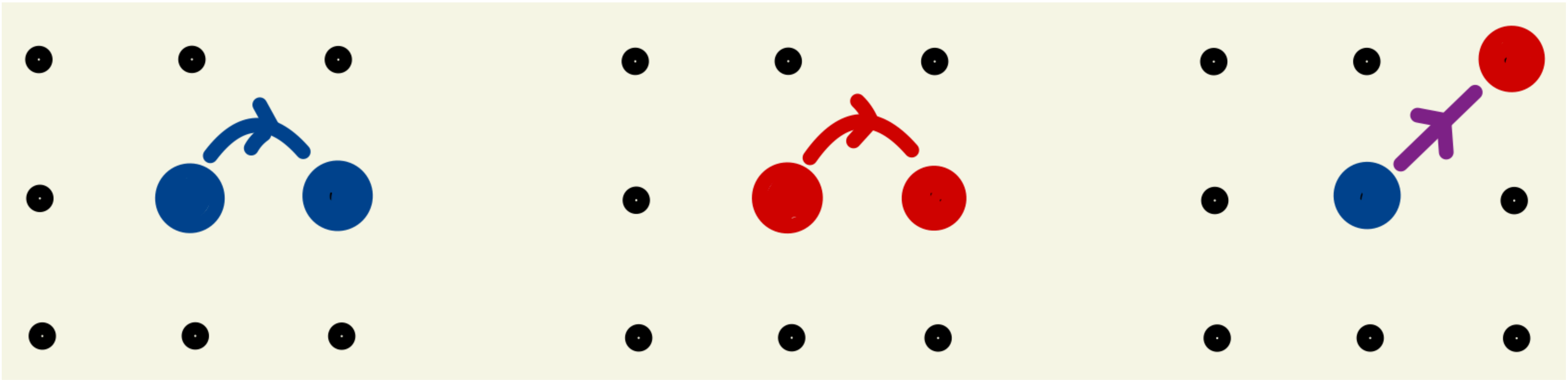
$$\vec{d} = \begin{pmatrix} \sin\theta\cos\phi \\ \sin\theta\sin\phi \\ \cos\theta \end{pmatrix}$$

Replace $\theta \in [0, \pi] \rightarrow k_x \in [0,2\pi]$

$\phi \in [0,2\pi] \rightarrow k_y \in [0,2\pi]$



3 independent hoppings



By construction, $||\vec{d}|| = 1$, gap/width$= \infty$

$$\theta \in [0,\pi] \rightarrow k_x \in [0,2\pi]$$

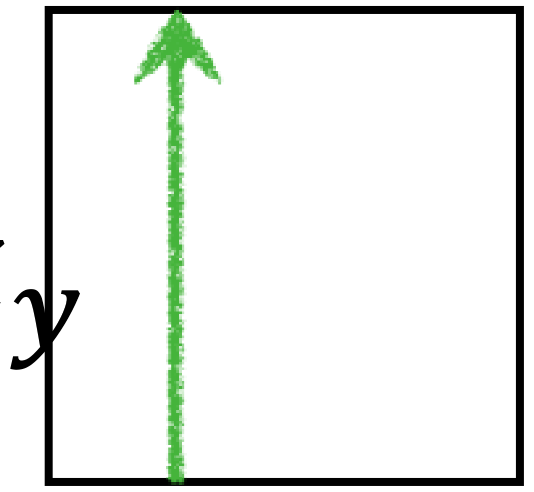
$$\phi \in [0,2\pi] \rightarrow k_y \in [0,2\pi]$$

$\vec{d}(\theta,\phi)$ covers sphere once as (θ,ϕ) are varied

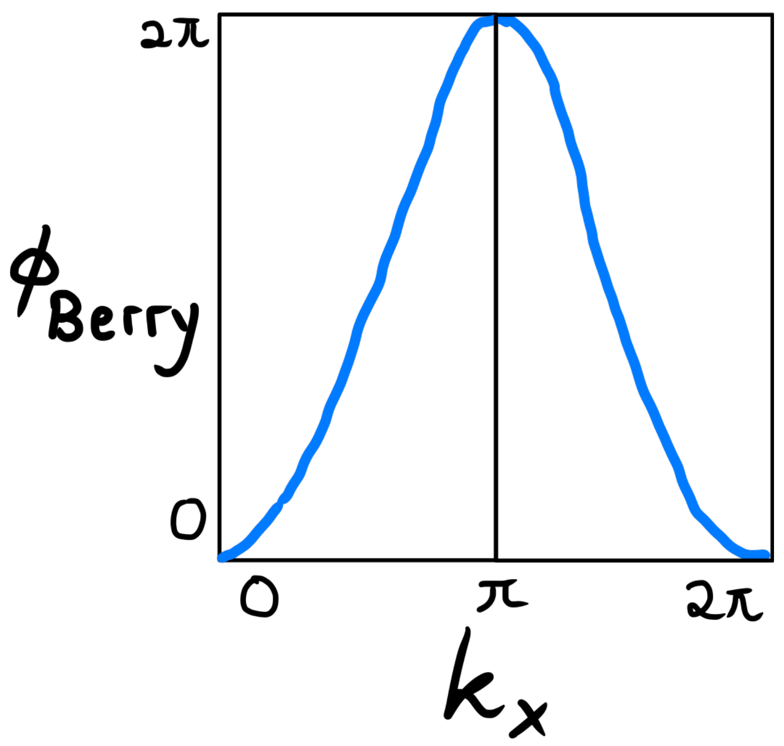
$\vec{d}(k_x,k_y)$ covers sphere once over $BZ/2(k_x > 0)$
and again over $BZ/2(k_x < 0)$ with opposite orientation

$\phi_{Berry}(k_x)$

k_y

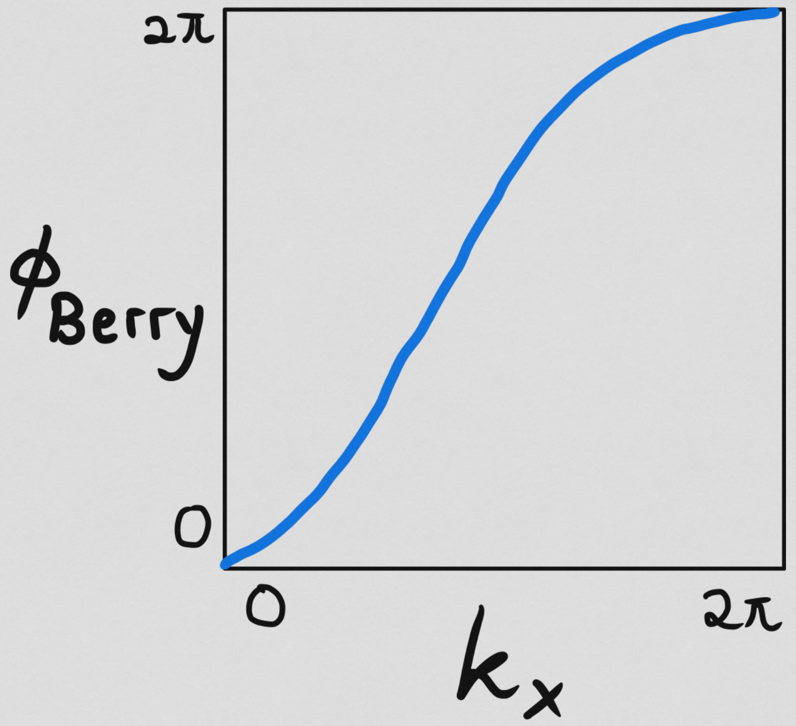


k_x



Reverting Thouless pump

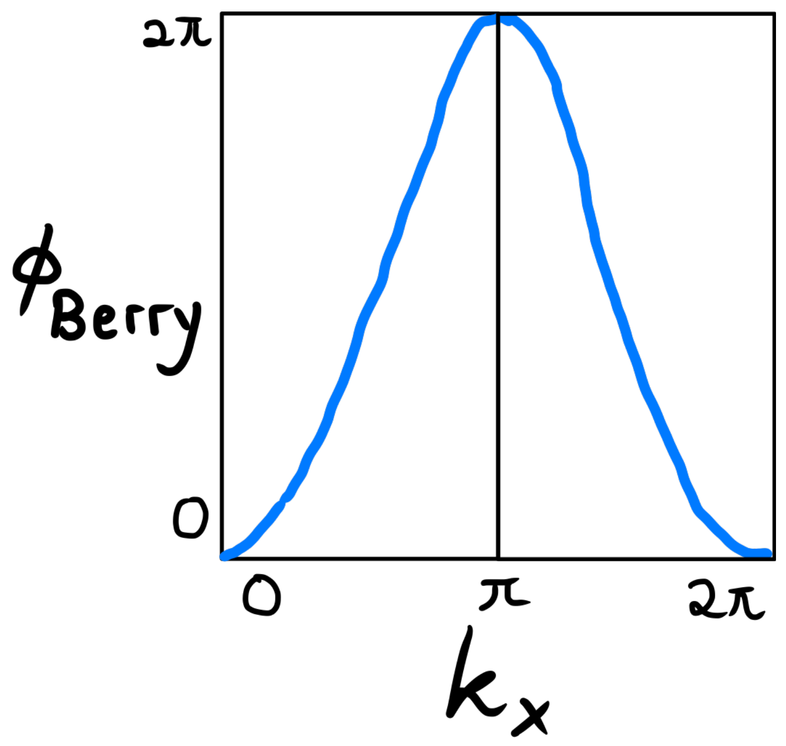
(compatible with T symmetry)



Thouless pump

(breaks T symmetry)

Reverting Thouless Pump



$$RTP_v = \frac{\phi_B(\pi) - \phi_B(0)}{2\pi} \in \mathbb{Z}$$

Quantization due to mirror symmetry

Rough argument: $k_x = 0$:

conduction-band wave function in one mirror rep.

valence: opposite mirror rep.

Wave functions can be chosen to be independent of k_y

$$A_v^y(0, k_y) = \langle u_v | i\partial_{k_y} u_v \rangle = 0 \Rightarrow \phi_B(0) = 0 mod 2\pi$$

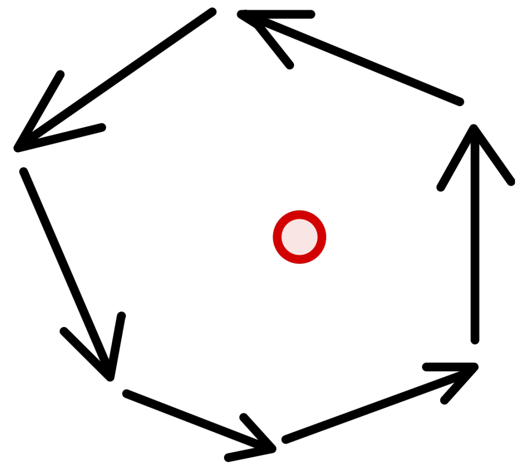
Same argument $\Rightarrow \phi_B(\pi) = 2\pi\mathbb{Z}$

<u>Interband component of obstruction invariant</u>

$$\vec{Field} = \vec{\nabla}_k phase[\boldsymbol{e} \cdot \boldsymbol{A}_{cv}]$$

Want $\vec{Field}$ to be topologically nontrivial and 'maximally' breaks centrosymmetry (P)

$$\oint \vec{Field} \cdot \vec{dk} = 2\pi\mathbb{Z}$$



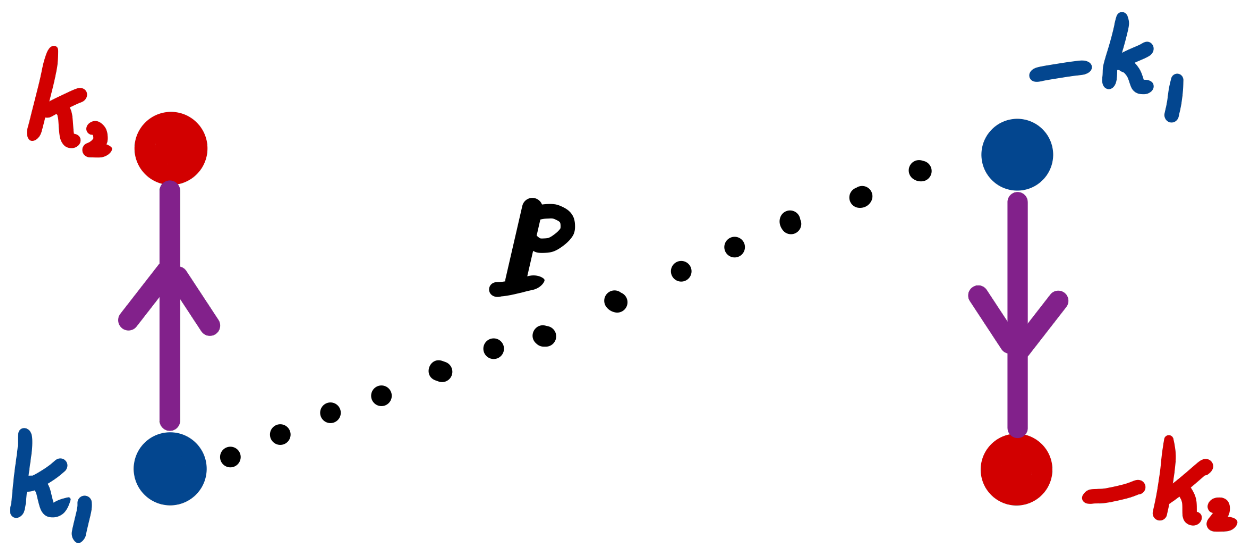
Optical vortex

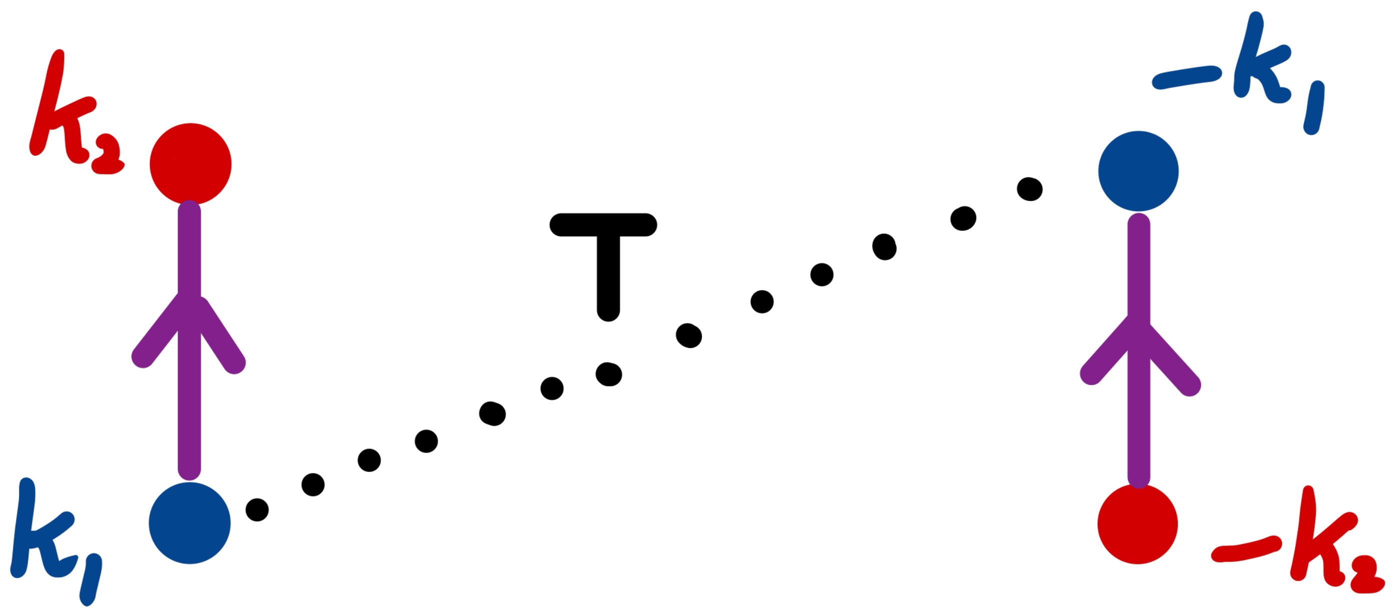
$$P: \boldsymbol{A}_{cv}(k) = \boldsymbol{A}_{cv}(-k)$$

maximally break centrosymmery

$$\boldsymbol{A}_{cv}(k) = \overline{\boldsymbol{A}_{cv}(-k)}$$

Compatible with T symmetry





Optical vorticity

Any vortex in T-symmetric system must break centrosymmetry

Vorticity invariant counts number of vortices in $BZ/2(k_x > 0)$

$$Vor = \oint_{\partial BZ/2} \frac{\vec{Field} \cdot \vec{dk}}{2\pi} \in \mathbb{Z}$$

To recapitulate, we have defined

$$Obs = -2RTP_v - Vor$$

which inputs the wave function, outputs an integer

Relate Obs to the shift vector

Define dimensionless shift by integrating over lines of constant k_x

$$\tilde{S^y}(k_x) = \int_0^{2\pi} S_{cv}^y(k_x, k_y)\frac{dk_y}{2\pi}$$

$$\tilde{S^y}(k_x) = 1 \Leftrightarrow \text{Average}[S_{cv}^y] = \text{lattice period } a$$

Claim: $\tilde{S^y}(\pi/a) - \tilde{S^y}(0) = Obs = -2RTP_v - Vor$

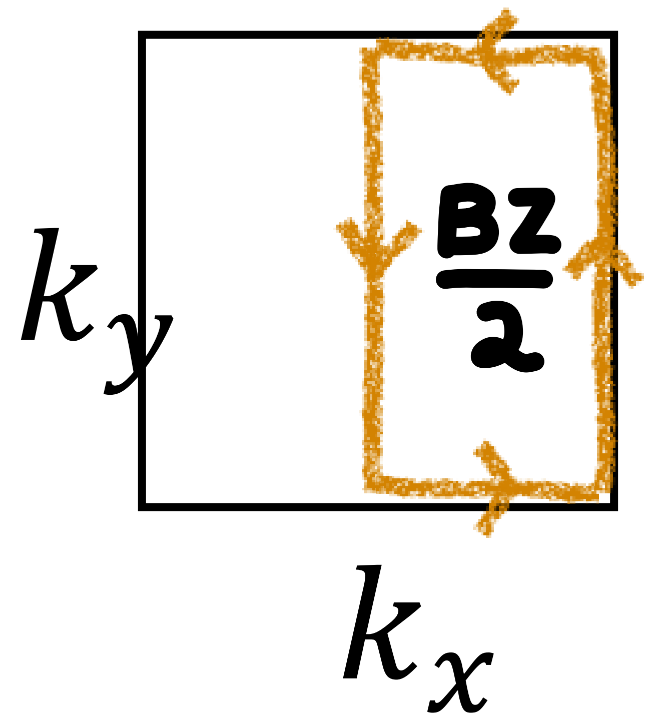
$Obs \neq 0 \Rightarrow$Quantized difference in shift vector

$\Rightarrow$ impossible to tune $S_{cv}^y(k) = 0$ for all k

(P1) Shift obstruction

Claim: $\tilde{S}^y(\pi/a) - \tilde{S}^y(0) = -2RTP_v - Vor$

$$\tilde{S}^y(\pi/a) - \tilde{S}^y(0) = \oint \frac{dk}{2\pi} \cdot \overbrace{\left(A_c(\boldsymbol{k}) - A_v(\boldsymbol{k}) - \nabla_k phase[e \cdot A_{cv}]\right)}^{S_{cv}(\boldsymbol{k})}$$



$$= \quad RTP_c - RTP_v \quad -Vor$$

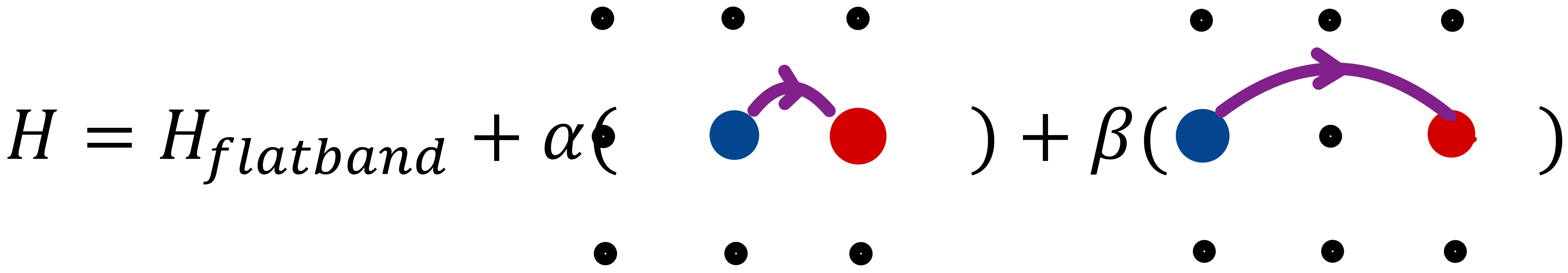
Observation: each of the dimensionless shifts is quantized

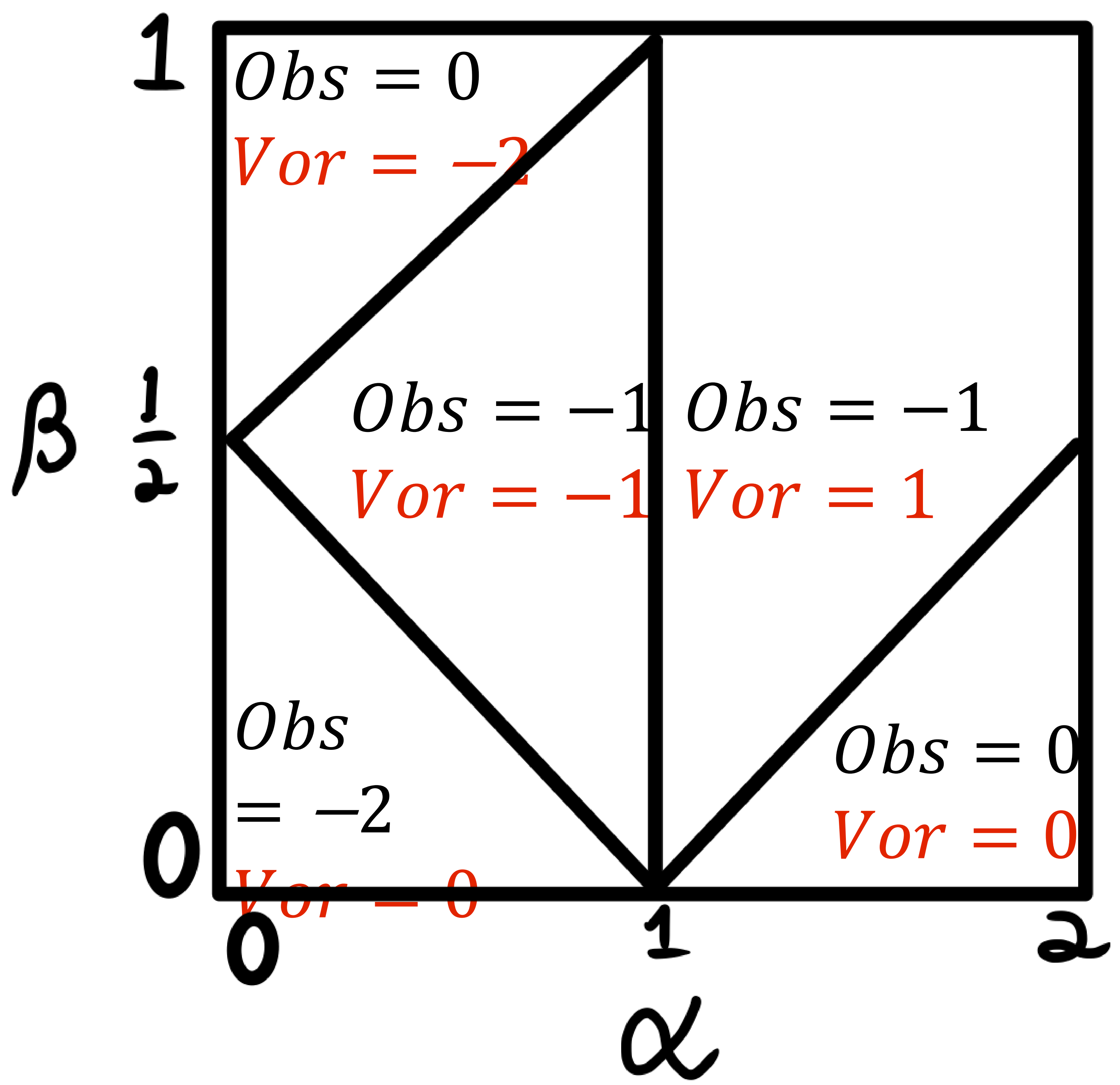
$$\tilde{S}^y(0) = \frac{\phi_B(0)}{2\pi} - \int \frac{dk_y}{2\pi} \partial_{k_y} phase[e \cdot A_{cv}] \in \mathbb{Z}$$

$$\tilde{S}^y(\pi) \in \mathbb{Z}$$

Proof that different phases (Obs,Vor) are realizable in models

Deform the flatband model with two parameters:





Want to prove (P2) Wide band gaps + large **transient** $j_{shift}(F^{yxx} \approx 10\mathbb{Z})$

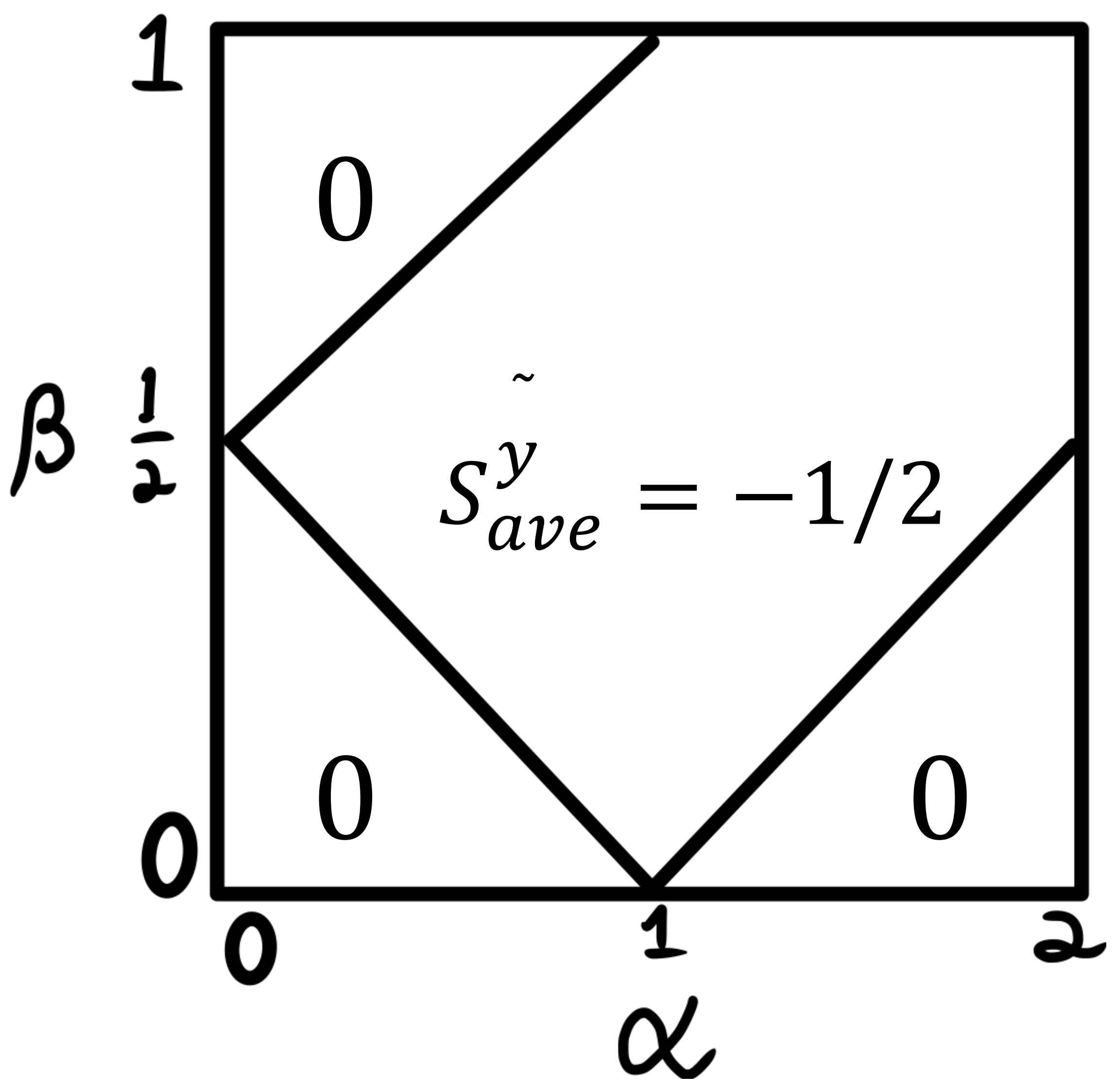
Reason for topological multiplier?

Argument:

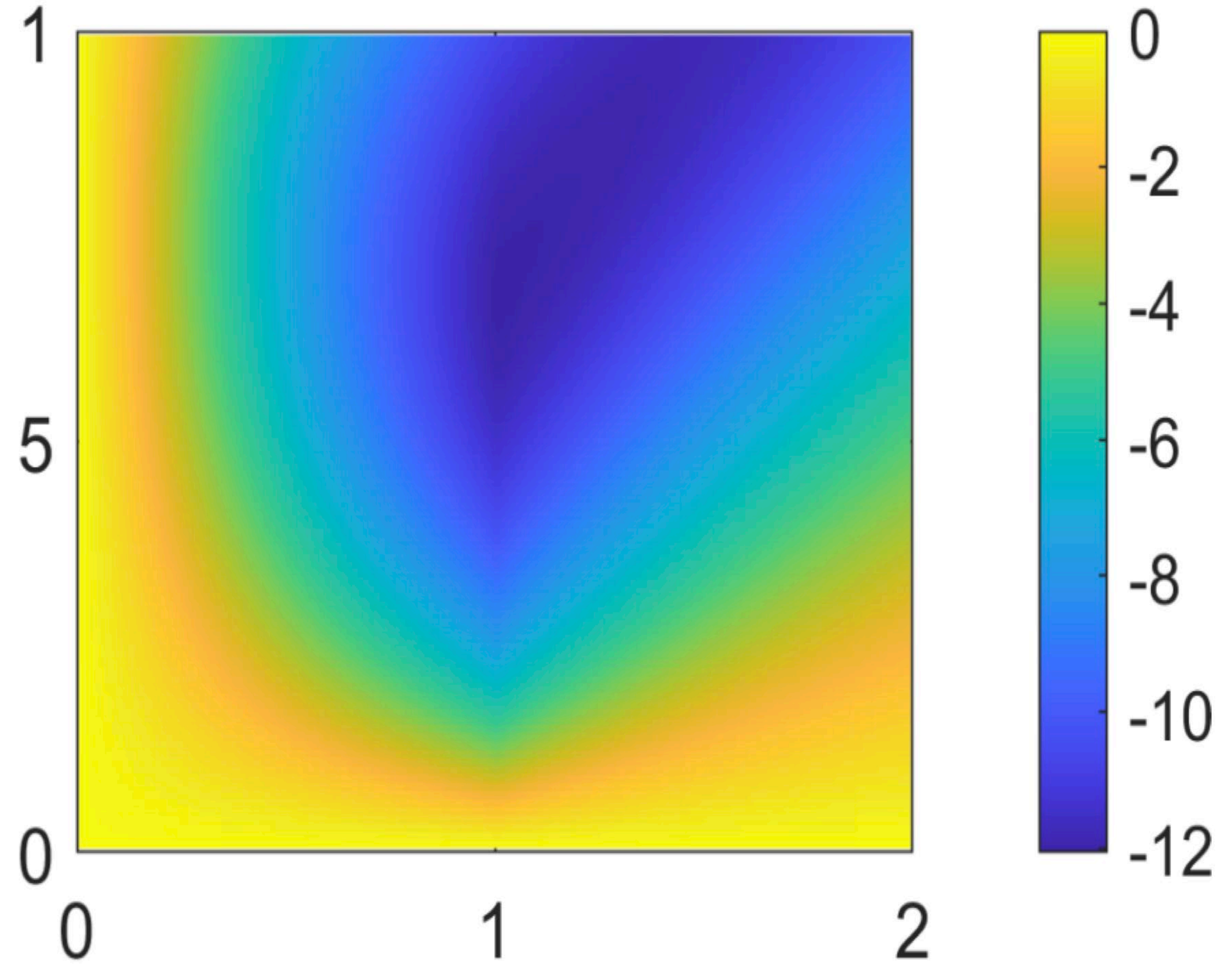
Average dimensionless shift = $\tilde{S}^{y}_{ave} = \frac{1}{2}[\tilde{S}^{y}(\pi/a) + \tilde{S}^{y}(0)] = \mathbb{Z}/2$

$F^{yxx} \doteq \int_{band\ width} \sigma^{yxx}_{Kubo} d\omega$ ~BZ average of $S^{y}_{cv}(k) \sim 2\pi\tilde{S}^{y}_{ave} \sim \pi\mathbb{Z}$

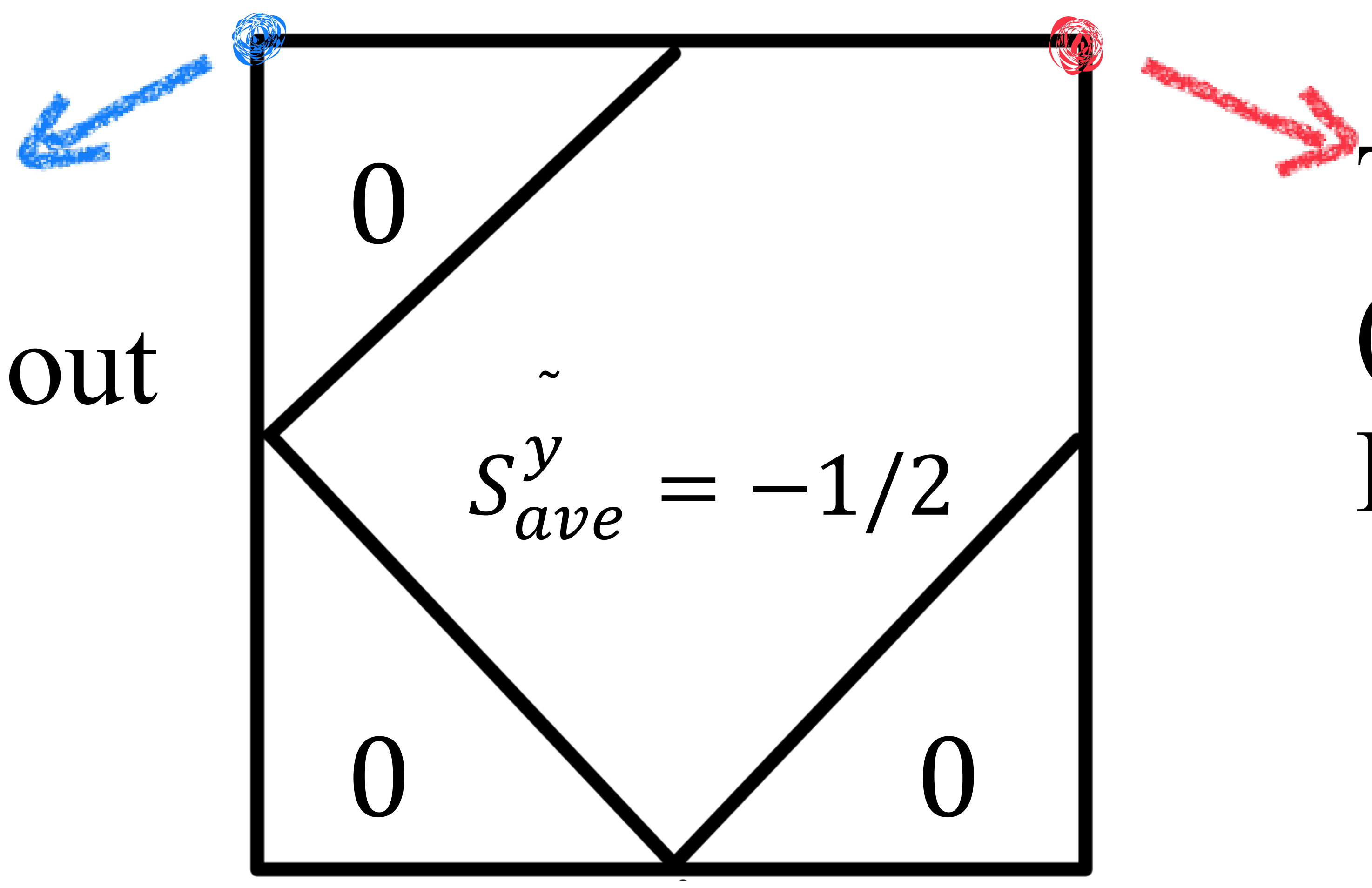
Numerical substantiation:



Color plot of F^{yxx}



Intra- and interband
Berry effects cancel out
=> small shift



Trivial intraband Berry phase
(trivial in all known classifications)
Large shift due solely to vorticity

A complete geometrical theory of shift current must treat the intra- and interband Berry connections on equal footing.

Previous geometrical theories: incomplete and non-topological

(Morimoto, Nagaosa 2016; Fregoso, Morimoto, Moore 2017)

Generalizations of intrinsically noncentric TI's for photovoltaics

Different symmetry: rotation-protected RTP (AA, Nelson, Soluyanov, 2021)

2-band → N-band Hamiltonians, subject to conditions on the symmetry reps. of *both* conduction and valence bands

Hallmark of 'symmetry-protected delicate topology'
(Nelson, Neupert, AA, Bzdusek, 2022)

not stable topology, not fragile
qualitatively distinct Wannier orbitals and surface states
(Nelson, Neupert, Bzdusek, AA, 2021)

Different intrinsically noncentric topo. invariant: Hopf (delicate)

All known delicate invariants are also intrinsically noncentric

Punchlines

A complete topological theory of the shift current:
treats the intra- and interband Berry connections on equal footing.

Only for intrinsically noncentric TI's can wave function topology => nontrivial shift
"Shift obstruction"

As a matter of principle, wide-gap TI's exist with large transient shift currents.

Only a handful of intrinsically noncentric TI's are known theoretically

Conjecture: many delicate noncentric TI's await to be discovered.

Opinion: one of the few intersections between fundamental topological theory
with promising technological applications

AA, arXiv:2203.11225, 2022