Quantitative relationship between polarization differences and the zone-averaged shift photocurrent

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A relationship is derived between differences in electric polarization between bands and the “shift vector” that controls part of a material’s bulk photocurrent, then demonstrated in several models. Electric polarization has a quantized gauge ambiguity and is normally observed at surfaces via the surface charge density, while shift current is a bulk property and is described by shift vector gauge invariant at each point in momentum space. They are connected because the same optical transitions that are described in shift currents pick out a relative gauge between valence and conduction bands. We also discuss subtleties arising when there are points at the Brillouin zone where optical transitions are absent. We conclude that two-dimensional materials with significant interband polarization differences should have high bulk photocurrent, meaning that the modern theory of polarization can be used as a straightforward way to search for bulk photovoltaic material candidates.

I. INTRODUCTION

Many electronic and optical properties of crystals depend not just on the energy band structure but on the detailed properties of Bloch wave functions. A simple example is that optical transitions in a solid, just like in an atom, involve matrix elements that depend on the symmetries of the underlying wave functions or orbitals. A deeper example is that the geometric or Berry phase of Bloch wave functions controls the electrical polarization and other properties. Although the spontaneous polarization of solids was already of interest to the ancients, and the polarization of a finite distribution of charge density is easily understood, the proper computation of electrical polarization from a unit cell of an infinite crystal had to await the “modern theory of polarization”,¹⁻⁴ which is now widely used in practical calculations.

The goal of the present paper is to explain the quantitative connection between bulk nonlinear optical properties of a material, specifically the shift current piece of photocurrent linear in the intensity of applied light, and electrical polarization. The shift current response is determined by a third rank tensor,

\[ J_{\text{shift}}^a = 2 \sum_b \sigma^{abb} E^b(\omega) E^b(-\omega), \]  

where the electric field is \( E^b(t) = E^b(\omega)e^{-i\omega t} + E^b(-\omega)e^{i\omega t} \). It is nonvanishing when inversion symmetry is absent, e.g., for ferroelectric materials. The tensor can be written in an intuitive way as (see Appendix A)

\[ \sigma^{abb} \approx \frac{e}{k} \sum_{nm} \int_{BZ} R_{nm}^{a,b} \epsilon_{2, nm}^{bb}, \]  

where \( \epsilon_{2, nm}^{bb}(k, \omega) \) is the diagonal (band-resolved) imaginary part of the density of states, and the integral over the Brillouin zone (BZ) in \( d \) dimensions. In the following we often suppress the frequency and momentum dependence of quantities for simplicity of notation. Importantly, the shift current includes a geometrical shift vector \( R_{nm}^{a,b} \) defined by,

\[ R_{nm}^{a} = \frac{\partial \phi_{nm}^b}{\partial k^a} + A_{nm}^a - A_{nm}^a, \]  

where \( A_{nm}^a = \frac{\partial \phi_{nm}^b}{\partial k^a} \) are the Berry connections

\[ A_{nm}^b = i\langle u_n | \frac{\partial}{\partial k^b} | u_m \rangle, \]  

and \( u_n \) is the periodic part of the Bloch wave function at wave vector \( k \). \( b = x, y, z \) is a Cartesian axis, and \( \phi_{nm}^b \) is the phase of the connection \( A_{nm}^b = |A_{nm}^b|e^{-i\phi_{nm}^b} \). The shift vector also determines the second harmonic generation and electro-optic responses of semiconductors.

We note that the definition of shift vector in (3) involves the gauge-dependent quantities \( A_{nm}^a, A_{nm}^b, \) and \( \phi_{nm}^b \). However, the combination is gauge invariant, at all points of the BZ where the optical transition matrix element \( A_{nm}^b \) is nonzero. Conversely, electrical polarization is written in the standard theory as an integral of the locally gauge-dependent Berry connection. In other words, the contribution of a particular \( k \)-point to the electrical polarization is not meaningfully defined. The total polarization is gauge dependent up to a quantized ambiguity; in the simplest case of one spatial dimension, the polarization

\[ e \int_{BZ} A_{nn} = P_n \]  

is defined only up to addition of an integer multiple of electron charge. For example, gauge transformations \( u_n \rightarrow e^{i\phi_n} u_n \) change \( P_n \) by \( je \), where \( j \in \mathbb{Z} \) is the winding number of the angular variable \( \phi_n \) around the BZ. The physical bulk polarization is defined as a difference with respect to an inversion-symmetric reference system which is adiabatically deformed with each other while keeping a fixed value of \( j \). Nevertheless, the (gauge-invariant) shift vector is directly related in many cases to (gauge-dependent) polarization differences between the valence and conduction band.
The shift current mechanism has recently gained interest for its potential novel optoelectronic applications based on ferroelectrics\textsuperscript{11–16}. In particular, 2D materials have highly tunable electronic and optical properties\textsuperscript{17–20} and are expected to generate large shift currents\textsuperscript{21–23}. We can identify three factors that determine the magnitude of the shift current: density of states, velocity matrix elements, and shift-vector matrix elements. In three dimensions, they are all intertwined with no obvious relation among them\textsuperscript{8}. In two dimensions, on the other hand, the density of states is constant and the optical transitions are determined by velocity and shift-vector matrix elements. Approximating the dipole matrix elements \( |p_{nm}|^2 \) by a constant \( \varepsilon_{bb} \) [see Appendix A Eq. (A1)] we obtain

\[
\sigma^{ab} \approx -\frac{\pi e^2 \varepsilon_{bb}}{\hbar^2} \sum_{nm} \int \delta(\omega_{mn} - \omega),
\]

where \( \hbar \omega_{nm} = \hbar \omega_n - \hbar \omega_m \) are band energy differences and \( f_{nm} = f_n - f_m \) differences of Fermi distribution functions of band \( n \) and \( m \). As pointed out in Ref. 23, in real-life applications such as solar cells, the integrated response over a frequency range is more important than the response at a single frequency. Integrating over all frequency,

\[
\int d\omega \sigma^{ab} \approx -\frac{\pi e^2 \varepsilon_{bb}}{\hbar^2} \sum_{nm} \int \delta(\omega_{mn} - \omega),
\]

we see that the total short-circuit current is proportional to the integrated shift vector over the BZ. As shown below, the integral of the shift vector over the BZ is equal to the polarization difference evaluated in a specific gauge; the optical transitions mediated by the shift vector can be viewed as fixing the relative gauge between valence and conduction bands, at least in the simplest case where such transitions are allowed at every \( k \)-point. This connection between polarization and shift vector indicates that materials with significant polarization differences between bands (minimized over gauge ambiguities) must have significant shift vectors somewhere in the BZ. In order to understand this relation we consider simple models first.

\section{II. Relationship Between Shift Vector and Polarization}

We start our analysis focusing on one-dimensional (1D) systems. Let us consider conduction and valence bands, which we label with \( c \) and \( v \), separated by an energy gap. In particular, we consider insulators with broken inversion symmetry that support nonzero polarization, where the wave functions and off-diagonal Berry connections are complex. In addition, we adopt the periodic gauge\textsuperscript{24,25} defined by \( \psi_n(k + G, r) = \psi_n(k, r) \) where \( \psi_n \) are Bloch wavefunctions and \( G \) a reciprocal lattice vector. In this case, all connections \( A_{nm} \) are periodic in the BZ, i.e., \( A_{cw}(k + G) = A_{cv}(k) \) (see Appendix B). Since the phases \( \phi_{cv}(k) \) at \( k \) and \( k + G \) coincide modulo 2\( \pi \), we can define winding \( W_{cv} \) of the phase \( \phi_{cv} \) around the BZ as

\[
W_{cv} = \frac{1}{2\pi} \oint d\phi_{cv} \in \mathbb{Z}.
\]

Here the winding \( W_{cv} \) can be any integer because we still have the freedom to perform transformations such that \( \partial_k \varphi_n \) is periodic, e.g., large gauge transformations that change the value of \( W_{cv} \) and keep \( \psi_n \) periodic over the BZ. We define the optical gauge by further constraining the periodic gauge such that \( \phi_{cv} = 0 \) and constant. When \( A_{cv} = 0 \) at some \( k \)-point in the BZ (which we call “optical zero”), the phase \( \phi_{cv} \) is not well-defined, and hence, \( W_{cv} \) is multivalued. The existence of optical zeros is physical and cannot be removed by gauge transformations.

Since \( R_{cv} \) is related to the shift of wave packets [see Fig. 1(a)], we can expect that an integral of \( R_{cv} \) over \( k \) has a relationship to the difference of polarization of the two bands. Indeed, integrating \( R_{cv} = \partial_k \phi_{cv} + A_{cc} - A_{cv} \),
The site potential, Fig. 1(a). Inversion symmetry is broken if \( \Delta \neq 0 \) and \( \delta \neq 0 \) and preserved otherwise (for details of the model, see Appendix D). The shift vector for this (and any two-band) model can be computed and studied analytically. For example its gauge invariance is made apparent when we write it in terms of the Hamiltonian and its derivatives (see Appendix C).

With a gauge in Eq. D3, we obtain \( W_{cv} = 0 \) [see Fig. 1(b)]. The shift vector \( \tilde{R}_{cv} \) is usually assigned the meaning of the size of the microscopic dipole formed by the photo-excited electron \( \gamma \). Since \( \tilde{R}_{cv} \) could grow without limit (see Appendix D), we believe, \( \tilde{R}_{cv} \) has a more well defined physical meaning, namely, as the distance between the valence and conduction centers of charge [Fig. 1(a)], and is therefore bounded by the lattice spacing \( \alpha \).

At \((ka, \delta) = (0,0)\) we have \( A_{cv} = 0 \), and the size of the discontinuity in \( \tilde{R}_{cv} \) [Fig. 1(b)] is determined by the vorticity associated with the optical zero as follows. We consider the parameter \( \delta \) as if it were a Cartesian direction and define the gauge invariant shift vectors as \( R_{cv}^{\mu} = \partial_{\mu} \phi_{cv} \) holds for all \( \alpha \). We used parameters \( B/A = 0.5, e = a = 1 \) and \( 0 < \epsilon \ll 1 \). In evaluating \( P_1 - P_2 \), we adopted the gauge given in Eq. (E4) with \( \varphi_n = 0 \).

leads to
\[
e R_{cv} = ea \int_{a_2} R_{cv} = ea W_{cv} + aP_c - aP_v, \tag{9}
\]
where \( P_{cv} \) is polarization of conduction and valence bands. Eq. (9) shows that the integral of the shift vector over the BZ is proportional to the polarization difference between the conduction and valence bands up to an integer \( W_{cv} \). In particular, the optical gauge allows us to directly connect shift vector and polarization as
\[
e R_{cv} = aP_c - aP_v \tag{10}
\]
since \( W_{cv} = 0 \). We emphasize that this is only possible when there is no optical zero in the region of the integral. Let us consider some explicit examples.

### III. RICE-MELE MODEL

Let us apply the above analysis to the Rice-Mele (RM) model \( \gamma \) [see Fig. 1(a)], which is an archetypal model of ferroelectricity along the polar axis. It applies to polyacetylene, BaTiO\(_3\), and even monochalcogenides \( \gamma \). It is given by
\[
\hat{H} = \sum_i [\frac{t}{2} + (-1)^i \delta \frac{\Delta}{2} c_i^\dagger c_{i+1} + h.c. + (-1)^i \Delta c_i^\dagger c_i]. \tag{11}
\]

The \( c_i \) (\( c_i^\dagger \)) annihilates (creates) s-wave electron states at site \( i \). The unit cell of size \( a \) has two sites; \( \delta \) parametrizes the dimerization of the chain and \( \Delta \) the staggered on-site potential, Fig. 1(a). Inversion symmetry is broken

\[W_{12} = 0 \quad W_{12} = 1 \quad W_{12} = -1\]

\[\alpha = 0.1 \quad \epsilon = 0.5 \quad 1.5 \quad 1 \quad 0.5 \quad -0.5 \quad -1 \quad -1.5 \quad \alpha \]

\[\frac{4\pi}{3} + \epsilon \quad \frac{5\pi}{3} - \epsilon \quad -\epsilon \quad 0 \quad (ae) \quad P_1 - P_2 \]

### IV. 1D THREE-BAND MODEL WITH INVERSION BREAKING

Next we show that the direct relationship between shift vector and polarization is not limited to the two band models by demonstrating the relationship in the case of general number of bands. As an example, we consider the three-band model described by
\[
\hat{H} = \sum_j t_j c_j^\dagger c_{j+1} + h.c., \tag{13}
\]
with \( t_j = A + B \cos (2\pi j/3 - \alpha) \). In this model the lower band pumps \(-2e\) while the other two pump \( e \) per cycle in \( \alpha \in [0, 2\pi] \). (For details of the model see Appendix E.) To be concrete, let us consider the lowest two bands \( n = 1, 2 \). As can be seen from Fig. 2, \( R_{12} \) has integer discontinuities at the values of \( \alpha \) for which \( A_{12} = 0 \) and \( \phi_{12} \) is not
well defined. The exact location of the discontinuities is determined by the vorticity of the field \( \mathbf{R}_{12} \) and whether it vanishes or not, see Appendix E.

V. TWO AND THREE DIMENSIONS

We have shown in detail how the integral of the shift vector is related to the electric polarization differences in 1D. We next consider generalizations to higher dimensional. In higher dimensions the shift vector has two or more Cartesian indices \( a, b = x, y, z \). The analogous definition to Eq. (8) is

\[
W_{nm}^{a,b} = \frac{R_{ab}}{l^a} \int_{BZ} \frac{\partial \phi_{nm}^{a,b}}{\partial k^a},
\]

(14)

where \( l^a \) is the primitive lattice vector component and \( v \) is the volume of the primitive unit cell. If we define the integral of shift vector over the BZ as

\[
\bar{R}_{nm}^{a,b} = v \int_{BZ} P_{nm}^{a,b},
\]

(15)

then we obtain

\[
e\bar{R}_{nm}^{a,b} = v(P_n^a - P_m^a) + W_{nm}^{a,b}vQ^a,
\]

(16)

where \( Q^a = el^a/v \) is the quantum of polarization along the \( a \) Cartesian axis. There are two situations of interest. First, if there are no optical zeros on the parameter space path, we can define an optical gauge where the polarization difference can be inferred from the integral of the shift vector with \( W_{nm}^{a,b} = 0 \). In this case, \( e\bar{R}_{nm}^{a,b} = v(P_n^a - P_m^a) \) holds and materials with large polarization differences (the right hand side) lead to efficient photovoltaic responses (through shift vector in the left hand side).

Second, if there exist optical zeros, the optical gauge has discontinuities. Then, \( W_{nm}^{a,b} \) is not quantized since a winding number \( \int dk_a \partial \phi_{nm}^{a,b} \) as a function of \( k_a \) \( (c \neq a) \) in general has jumps at optical zeros. In this case, while we cannot directly relate \( \bar{R}_{nm}^{a,b} \) and \( P_n^a - P_m^a \), the right hand side including \( W_{nm}^{a,b} \) can be evaluated in a fairly easy way, providing a guideline to search efficient photovoltaic materials. In particular, Eq. (16) shows that the polarization differences and locations of optical zeros (that determine \( W_{nm}^{a,b} \)) are important in understanding photovoltaic responses in the left hand side.

As an example, consider a simple extension of the RM model to two dimensions. It consists of two 1D RM models, one in the \( x \) direction and the other in the \( y \) direction, with dimerization parameters, \( \delta_x, \delta_y \). We suppose that the staggered potential is modulated along \( x \) but constant along \( y \). It is easy to show that the electrical polarization is along \( x \) and only transitions from bands \( 1 \to 3 \) and \( 2 \to 4 \) are allowed. There is a line of optical zeros at \( (k_x, k_y, \delta_x) = (0, k_y, 0) \) for all \( k_y \) and one can define gauge-invariant fields in the plane \( (k_x, \delta_x) \) with similar vorticity as in Fig. 1(c). As long as \( \delta_x \neq 0 \) the winding \( W_{12}^{xx} \) = 0. Similarly to the RM model in 1D, the existence of the singularity at \( \delta_x = 0 \) gives rise to a discontinuity of \( \bar{R}_{12}^{xx} \).

VI. DISCUSSION AND CONCLUSIONS

We demonstrated that the integral of the shift vector is a dominant factor in determining the total shift current generated in 2D materials. Barring points where the optical transitions are forbidden, the integral of the shift vector has the meaning of polarization differences between conduction and valence bands. We also describe the theoretical tools for analyzing the polarization differences in the presence or absence of optical zeros. With the caveats explained above, Eq. (7) gives

\[
\int d\omega \sigma_{aa} \approx -\frac{\pi e^2 \varepsilon_{aa}}{h^2} \sum_{nm}(P_n^a - P_m^a),
\]

(17)

where we assumed the optical gauge and zero temperature where \( f_{nm} = -1 \) for \( n(m) \) a conduction (valence) band and = 1 when \( n(m) \) a valence(conduction) band. The short-circuit current on a device is proportional to the sum of polarization differences. Since the electronic part of the spontaneous polarization is the sum over all occupied (valence) band polarizations, Eq. (17) suggests that 2D ferroelectrics are natural candidates for materials with large shift-current generation. Hence, our results provide the long-sought link between electric polarization and shift current.

There is numerical evidence that 2D ferroelectric single-layer IV monochalcogenides have large shift current. A recent experiment measuring shift current on thin films of GeS is consistent with our results. We also expect large shift current in the recently discovered 2D ferroelectric SnTe. Finally, the right-hand side of Eq. 16 is easier to evaluate than the left-hand side with standard \( ab \) initio methods and serves as an estimate of shift current generation and provides a practical guideline to search for materials with large shift currents.

VII. ACKNOWLEDGMENTS

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Appendix A: Phase-independent expression of shift vector

The shift current tensor, Eq. (2) in the main text, in d dimension is usually written as

$$\sigma^{a;b}(0; \omega, -\omega) = \frac{i\pi e^3}{2\hbar^2} \int_{BZ} \sum_{nm} f_{nm} (r_{nm}^b c_{nm;a} + r_{nm}^c b_{nm;a}) \delta(\omega_{mn} - \omega),$$  \hspace{1cm} (A1)

Here we defined the integral as $\int_{BZ} \equiv \int d\mathbf{k}/(2\pi)^d$ over the Brillouin zone (BZ) in d dimensions for notational convenience. $\hbar\omega_{mn} = \hbar\omega_n - \hbar\omega_m$ are band energy differences and $f_{nm} = f_n - f_m$ are differences of Fermi distribution functions of band $n$ and $m$. The dipole matrix elements $r_{nm}^a$ and generalized derivatives are

$$r_{nm}^b \equiv A_{nm}^b \quad [n \neq m \text{ and } 0 \text{ otherwise}]$$ \hspace{1cm} (A2)

$$r_{nm;a}^b \equiv \frac{\partial r_{nm}^b}{\partial k^a} - i(A_{nm}^a - A_{nm}^b) r_{nm}. $$ \hspace{0.2cm} (A3)

$A_{nm}^b = i\langle u_n | \frac{\partial}{\partial k^b} | u_m \rangle$ are the Berry connections, $\hbar\omega_{nm} = \hbar\omega_n - \hbar\omega_m$ are the band energies and $f_{nm} = f_n - f_m$ are the fermionic occupation numbers. We can write $A_{nm}^b = v_{nm}/i\omega_{nm}$, for nondegenerate bands where $v_{nm}^b$ is the velocity matrix element. Setting $b = c$ for linear polarization and using polar representation, $r_{nm}^a = |r_{nm}^a| e^{-i\phi_{nm}^a}$, Eq. (A1) reduces to

$$\sigma_{a;b}(0; \omega, -\omega) = -\frac{\pi e^3}{\hbar^2} \int_{BZ} \sum_{nm} f_{nm} R_{nm}^{a;b} |r_{nm}^b|^2 \times \delta(\omega_{mn} - \omega),$$ \hspace{0.2cm} (A4)

where $R_{nm}^{a;b}$ is the so-called shift ‘vector’,

$$R_{nm}^{a;b} = \frac{\partial r_{nm}^b}{\partial k^a} + A_{nm}^a - A_{nm}^b.$$ \hspace{0.2cm} (A5)

An alternative expression for the shift vector, which avoids the use of $\phi_{nm}^b$, can be obtained from Eq. (A1). Since $\sigma_2(0; \omega, -\omega)$ is real we have

$$R_{nm}^{a;b} |r_{nm}^b|^2 = -\text{Im}[r_{nm}^b r_{nm;a}], $$ \hspace{0.2cm} (A6)

The right-hand-side is gauge invariant and has simple analytical expressions for effective models of monochalcogenides\textsuperscript{22,23}. It contains two important physical effects, density of states and the geometry of Bloch wave functions. To disentangle these effects, let us consider the case where $r_{nm}^b \neq 0$ (equivalently $v_{nm}^b \neq 0$) then the shift vector itself is well defined,

$$R_{nm}^{a;b} = -\frac{1}{|r_{nm}^b|^2} \text{Im}[r_{nm}^b r_{nm;a}], $$ \hspace{0.2cm} (A7)

and independent of the density of states. In the independent-particle approximation, the imaginary part of the dielectric function,

$$\epsilon_2^{ab}(\omega) = \epsilon_0 \frac{\epsilon_2}{\epsilon_0} \delta_{ab} - \frac{\epsilon_2}{\epsilon_0} \int_{BZ} \sum_{nm} f_{nm} r_{nm}^a r_{nm}^b \delta(\omega_{mn} - \omega). $$ \hspace{0.2cm} (A8)

is dominated by the second term and comparing with Eq. (A4) we obtain Eq. (2) in the main text.

Appendix B: The optical gauge

The solutions of the Schrodinger equation with a periodic potential are Bloch wavefunctions,

$$\psi_n(\mathbf{k}, \mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{n}(\mathbf{k}, \mathbf{r}),$$ \hspace{0.2cm} (B1)

where $n$ is the bands index and $\mathbf{k}$ the crystal momentum. $u_{n}(\mathbf{k}, \mathbf{r} + \mathbf{R}) = u_{n}(\mathbf{k}, \mathbf{r})$ is the cell periodic part of the wave function and $\mathbf{R}$ is a lattice vector. The solutions of the Schrodinger equation are invariant under phase transformations $[U(1)$ gauge transformations$],$

$$\psi'_n(\mathbf{k}, \mathbf{r}) = e^{i\varphi_n(\mathbf{k})} \psi_n(\mathbf{k}, \mathbf{r}).$$ \hspace{0.2cm} (B2)

Under gauge transformations the Berry connections transform as

$$A_{nm}^b = A_{nm}^b e^{i(\varphi_m - \varphi_n)}$$ \hspace{0.2cm} (B3)

$$A_{nm}^{b;m} = A_{nm}^{b;m} - \frac{\partial \varphi_n}{\partial k^b}. $$ \hspace{0.2cm} (B4)

The diagonal matrix elements can change by an arbitrary phase $\varphi_n$. Hence choosing the diagonal elements is equivalent to fixing a particular gauge. On the other hand, the off-diagonal Berry connections transform as operators and therefore, if $A_{nm}^b = 0$ in one gauge it vanishes in all gauges. The dipole matrix elements and its generalized derivatives transform as operators

$$r_{nm}^b = e^{i(\varphi_m - \varphi_n)} r_{nm}^b$$ \hspace{0.2cm} (B5)

$$r_{nm;a}^b = e^{i(\varphi_m - \varphi_n)} r_{nm;a}^b,$$ \hspace{0.2cm} (B6)

but the standard derivative $\partial r_{nm}^b / \partial k^a$ does not transform as a tensor. From these results we see that the shift vector, Eq. (A7), is gauge invariant. Now, the Bloch states at $\mathbf{k}$ and $\mathbf{k} + \mathbf{G}$, with $\mathbf{G}$ a reciprocal lattice vector, are physically equivalent states. They can differ at most by a phase $\lambda$,

$$\psi_n(\mathbf{k} + \mathbf{G}) = \lambda \psi_n(\mathbf{k}),$$ \hspace{0.2cm} (B7)

where $\lambda = e^{i\varphi_n(\mathbf{k}, \mathbf{G})}$ is determined by the choice of $\varphi_n$. For arbitrary $\lambda_n$ the connections at $\mathbf{k}$ and $\mathbf{k} + \mathbf{G}$ are related as

$$A_{nm}^b(\mathbf{k} + \mathbf{G}) = A_{nm}^b(\mathbf{k}) + \lambda_n^* \frac{\partial \lambda_n}{\partial k^b},$$ \hspace{0.2cm} (B8)

$$A_{nm}^{b;m}(\mathbf{k} + \mathbf{G}) = \lambda_n^* A_{nm}^{b;m}(\mathbf{k}).$$ \hspace{0.2cm} (B9)

In general, the off-diagonal elements at $\mathbf{k}$ and $\mathbf{k} + \mathbf{G}$ differ by an arbitrary phase, but if we choose the periodic gauge where $\lambda_n = 1$, then both the Bloch wave functions and connections (diagonal and off-diagonal) are periodic.
Note that the phases at \( \mathbf{k} \) and \( \mathbf{k} + \mathbf{G} \) may differ by an integer multiple of \( 2\pi \). The ambiguity in \( A_i^b \) gives rise to an integer ambiguity in the polarization and the ambiguity in \( A_{nm}^b \) to the interband winding number \( W_{nm}^b \) described in the main text. This is because we still have freedom to impose gauge transformations in which \( \nabla \mathbf{k} \phi(\mathbf{k}) \) is periodic\(^{25} \), which include large gauge transformations. Let us call the subset with \( W_{nm}^a = 0 \) the optical gauge.

**Appendix C: Shift vector of two-band model from Hamiltonian derivatives**

For a two-band Hamiltonian given in first quantization as \( H = \sum_i d_i \sigma^i \), where \( d = (d_x, d_y, d_z) \), the right-hand side of Eq. (A6) is

\[
\text{Im}[r_{12}^b] = \epsilon_{nm} \left[ \frac{1}{4E_3} \left( d_m d_{i,a} d_{j,b} d_{i,a} - E^2 d_m d_{i,a} d_{j,ab} \right) \right] - E^2 d_m d_{i,a} d_{j,ab}.
\]

Appendix D: Shift vector and current in Rice-Mele model

In this section the shift vector and shift current for the Rice-Mele model of ferroelectrics is computed. The Hamiltonian is

\[
\hat{H}_{RM} = \sum_i \left( \frac{t}{2} - \frac{1}{2} \delta \right) (c_{i+1}^c c_i^v + h.c.) + (-1)^i \Delta c_i^c c_i^v,
\]

where \( c_i^c (c_i^v) \) destroys (creates) electron states at site \( i \), \( \delta \) parametrizes the dimerization of the chain, and \( \Delta \) is the staggered potential on sites A and B. If \( \Delta \neq 0 \), and \( \delta \neq 0 \) inversion symmetry is broken. The unit cell (of length \( a \)) has two sites. We obtain the Bloch Hamiltonian,

\[
H_{RM} = \sum_i d_i \sigma_x t \cos ka/2 - \sigma_y \delta \sin ka/2 + \sigma_z \Delta
\]

and eigenfunctions,

\[
u_c = \frac{e^{i\varphi_c}}{\sqrt{2}} \left( \frac{u}{u\epsilon^{i\varphi}} \right), \quad \nu_v = \frac{e^{i\varphi_v}}{\sqrt{2}} \left( \frac{u}{-u\epsilon^{i\varphi}} \right),
\]

where \( H_{RM} \nu_c,v = \pm E \nu_c,v, \phi = \arctan\left(\delta/t \tan(ka/2)\right) \) (mod \( \pi \)) is the azimuthal angle of the vector \( H_{RM} \) in the Bloch sphere, \( u = \sqrt{1 - \Delta^2/\bar{E}}, v = \sqrt{1 + \Delta^2/\bar{E}} \), and the eigenvalues are given by \( E = (t^2 \cos^2 ka/2 + \delta^2 \sin^2 ka/2 + \Delta^2)^{1/2} \) for the conduction and \( -\bar{E} \) for the valence band (\( \phi \) should not be confused with \( \varphi_{cn} \). We have added a gauge dependence \( \varphi_{cn} \) (\( n = c,v \)). The Berry connection will depend explicitly on the gauge used but results on the shift vector/current are gauge independent. In this section we choose \( \partial_k \varphi = 0 \). The Bloch wave functions are

\[
\psi_n(k,r) = \sum_j e^{ika z} [u_n^c(k) \chi(r-a_j) + e^{ika z} w_n^v(k) \chi(r-a_j-a/2)],
\]

where \( \chi \) are the atomic wave functions and \( u_n^c,v, w_n^c,v \) projections of the eigenfunctions on site A,B. The Berry connections,

\[
A_{nm} = i u_n^c \partial_k u_m^v - \frac{at\delta(E+\Delta)}{4E(E^2 - \Delta^2)} \quad (n = c,v)
\]

\[
A_{cv} = i \frac{u_c^v}{2} \partial_k u_v^v - \frac{a}{8E^2 \sqrt{E^2 - \Delta^2}} \left[ \Delta(t^2 - \delta^2) \sin ka \right. + \left. 2i\delta E \right]
\]
are both periodic with period $2\pi/a$. We define the phase \( \delta \phi_{cv} \) by $A_{cv} = |A_{cv}|e^{i\delta \phi_{cv}} = |A_{cv}|(\cos \delta \phi_{cv}, -\sin \delta \phi_{cv})$, and its derivative is

$$
\frac{\partial_k \delta \phi_{cv}}{2E} = \frac{\Delta}{2E} \frac{a\delta(t^2 - t^2)}{[\Delta^2(\delta^2 - t^2)^2 \sin^2 ka + 4\delta^2t^2E^2]}.
$$

This expression is smooth for $\delta \neq 0$. If $\delta = 0$ it can be seen that $A_{cv} = 0$ at $ka = 0, \pi$. The shift vector,

$$
R_{cv} = \frac{\partial_k \delta \phi_{cv}}{2E} + A_{cv} - A_{cv},
$$

can be computed analytically as

$$
R_{cv} = \frac{\Delta}{2E} \frac{a\delta(t^2 - t^2)}{[\Delta^2(\delta^2 - t^2)^2 \sin^2 ka + 4\delta^2t^2E^2]}
- \frac{\Delta}{2E} \frac{a\delta}{(E^2 - \Delta^2)}.
$$

Some observations about the behavior of the shift vector in the RM model are in order: (a) Generally, the shift vector does not vanish. (b) The shift vector is peaked at $ka = 0$ or $ka = \pi$, and (c) the shift vector can exceed the lattice spacing $a$. To illustrate this consider some limiting values of the shift vector,

$$
R_{cv}\big|_{\text{lim } k \rightarrow 0} = -\frac{a\Delta}{2\sqrt{t^2 + \Delta^2}}|_{\text{lim } \delta \rightarrow 0} = \infty
$$

$$
R_{cv}\big|_{\text{lim } k \rightarrow \pi/a} = -\frac{a\delta}{2t\sqrt{t^2 + \Delta^2}}|_{\text{lim } \delta \rightarrow 0} = 0
$$

$$
R_{cv}\big|_{\text{lim } \delta \rightarrow \epsilon} = -\frac{a\Delta}{2\sqrt{t^2 + \Delta^2}}|_{\text{lim } \Delta \rightarrow 0} = -a\Delta/2t
$$

(flattened band limit).

Hence one can check that at $ka = \pi$ the field $R_{cv} = (R_{cv}^{kk}, R_{cv}^{\delta k})$, defined in the main text, vanishes and at $ka = 0$ it diverges.

**Shift current.**- If the electric field is along the chain, e.g., the $z$ direction, the shift current is

$$
J_{\text{shift}}(\omega) = 2\sigma^{zzz}(0; \omega, -\omega)E^z(\omega)E^z(-\omega).
$$

For the two-band model this reduces to

$$
\sigma^{zzz}(0; \omega, -\omega) = e^3 \int_0^{2\pi/a} dk \frac{|\langle u_\omega | v^z | u_\omega \rangle|^2 R_{cv}}{\hbar^2 \omega^2} \delta\left( \frac{2E}{\hbar} - \omega \right)
$$

(D12)

where the matrix elements of the velocity operator $v^z = -i\hbar^{-1}\partial H_{RM}/\partial k$ are

$$
|\langle u_\omega | v^z | u_\omega \rangle|^2 = \frac{a^2}{16\hbar^2 E^2(2E^2 - \Delta^2)} \left( \Delta^2 \sin^2 ka + 4t^2 \delta^2 E^2 \right).
$$

The shift vector and the matrix elements of the velocity each have complicated expressions but the combination (the ‘integrand’),

$$
\frac{\hbar^2}{4E^2} |v_{cv}^z|^2 R_{cv} = |v_{cv}^z|^2 R_{cv} = -\text{Im}[r_{cv}^z r_{cv}^{z*}],
$$

is simply

$$
\text{Im}[r_{cv}^z r_{cv}^{z*}] = \frac{a^3 \delta \Delta}{32E^3}.
$$

(D15)

For $\delta \ll \Delta$, $R_{cv}$ is sharply peaked at $ka = 0$ but $|v_{cv}^z|$ peaks at $ka = \pi$. As $\delta$ increases in $R_{cv}$ and $|v_{cv}^z|^2$ broadens but their peaks’ maximum also decreases. The dependence on the velocity matrix elements (imaginary part of the dielectric function) is very prominent here because the system is 1D. The analytical expression for the shift current of the RM model simplifies to

$$
\sigma^{zzz}(0; \omega, -\omega) = -\frac{e^3 a^3 \delta \Delta}{8\hbar^3 \omega^3} \sum_i \frac{1}{|\partial_k E(k_i)|},
$$

(D16)

where $\partial_k E = a(\delta^2 - t^2) \sin ka / 4E$ is the velocity at momentum $k$ and $k_f$ are the two solutions of $2E(k_f) = h\omega$ for $h\omega > 2E$. In 1D, $\sigma^{zzz}$ diverges as $\omega^{-3}(2E - h\omega)^{-1/2}$ at the band edge, but is suppressed in 2D, where the role of the shift vector becomes prominent.
Appendix E: Polarization and shift vector in a three-band model

Let us consider the 1D model Hamiltonian

$$\hat{H}_{sb} = \sum_j t_j c_j^\dagger c_{j+1} + h.c., \quad (E1)$$

with $t_j = A + B \cos(2\pi j/3 - \alpha)$. There are three distinct values of the hoppings $t_j = t_1, t_2, t_3$. Hence, the unit cell (of size $a$) has three nonequivalent sites. The crystal has inversion symmetry for $\alpha = 0, \pi/3, 2\pi/3$, and $\pi, 4\pi/3, 5\pi/3$, when two of the hoppings are equal. The Bloch Hamiltonian is

$$H_{sb} = \begin{bmatrix} 0 & t_1 e^{ika/3} & t_3 e^{-ika/3} \\ t_1 e^{-ika/3} & 0 & t_2 e^{ika/3} \\ t_3 e^{ika/3} & t_2 e^{-ika/3} & 0 \end{bmatrix}. \quad (E2)$$

The eigenvalues and eigenvectors, $H_{sb} u_n = E_n u_n$, are

$$E_n = 2t_r \cos\left(\frac{1}{3} \arccos\left(\frac{t_3^2 \cos(ka)}{t_1^2} - \frac{2\pi n}{3}\right)\right), \quad (E3)$$

where $(n = 1, 2, 3)$ and we defined the root mean square and geometric average $t_r = \sqrt{(t_1^2 + t_2^2 + t_3^2)/3}$ and $t_g = (t_1 t_2 t_3)^{1/3}$ respectively, and

$$u_n = \frac{e^{i\varphi_n}}{N_n} \begin{bmatrix} E_n^2 - t_3^2 \\ t_2 t_3 e^{2ika/3} + E_n t_1 e^{-ika/3} \\ t_2 t_3 e^{-2ika/3} + E_n t_1 e^{ika/3} \end{bmatrix}, \quad (E4)$$

where $\varphi_n$ is chosen to enforce the periodic gauge. The normalization is $N_n = |(E_n^2 - t_3^2) + (t_2^2 - E_n^2) + (t_1^2 - E_n^2)(t_3^2 - E_n^2)|^{1/2}$. Using these wave functions, the Berry connections are calculated analytically as,

$$A_{nn} = \frac{a}{2N_n^2} (E_n^2 + 2t_2^2)(t_1^2 - t_3^2) - i \frac{a}{N_n^2} \left[ 3E_n (\partial_k E_n)(E_n^2 - t_2^2) + 2a E_n t_3^2 \sin(ka) \right], \quad (E5)$$

$$A_{nm} = \frac{a}{3N_n N_m} (E_n E_m + 2t_2^2)(t_1^2 - t_3^2) + i 2a t_3^2 (E_n^2 + E_m^2 + E_n E_m - 3t_2^2) \sin(ka) \frac{1}{3N_n N_m (E_n - E_m)}. \quad (E6)$$

Note that the Berry connections are periodic in $k$ space with period $G = 2\pi/a$. One can check that the optical zeros of $A_{12}$ are $\alpha = 0, 2\pi/3, 4\pi/3$, where $A_{12}(ka = \pi, \alpha)$ vanishes and hence the phase of $\phi_{12}$ is not well defined. In Figs. 3(a) and (b) we show the windings of the interband connection $A_{12}$ and the gauge-invariant vorticity of the optical zeros in the field $R_{12}$ described in the main text.

Polarization.- The polarization is given by the integral over the Berry connection as

$$P_n(\alpha) = \frac{1}{2\pi} \int dk A_{nn}(k, \alpha). \quad (E7)$$

In Fig. 3(a) we show the individual band polarizations as a function of $\alpha$. Note that the sum $P_1 + P_2 + P_3 = \pm 1$ (mod $e$), as expected. Also, the total charge pumped of band $n$ per cycle is

$$c_n(\alpha) = \int_0^\alpha d\alpha \int \frac{dk}{2\pi} \frac{\Omega_{k,\lambda}^n}{2\pi} = \int_0^\alpha d\alpha \int \frac{dk}{2\pi} i[\partial_k u_n | \partial_\lambda u_n ] - (\partial_\lambda u_n | \partial_k u_n )]$$

(E8)

One can check the charge pumped across the unit cell is $c_1(2\pi) = -2e$ and $c_{2,3}(2\pi) = +e$.

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